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POLYCYCLIC AROMATIC HYDROCARBONS: SOURCES, FATE AND LEVELS IN AIR, WATER, SOIL, SEDIMENTS, SLUDGE AND FOOD IN ONTARIO

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EXECUTIVE SUMMARY

This report covers a review of literature information on polycyclic aromatic hydrocarbons (PAH), primarily in Ontario. Specifically, this report deals with chemical and physical properties of PAH as well as the sources, inputs and fate of PAH to the environment.

Good, reliable data for PAH physical properties are scarce. For example, recorded vapour pressure data frequently range over several orders of magnitude and solubility data in solvents other than water are often non-existent. Similarily, reliable, chemical reactivity data are equally scarce.

The report discusses the sources and input to the environment by compiling the emission factors and profiles for point and non-point sources in Ontario. Based on the atmospheric emissions inventory for these compounds, it is estimated that the major PAH sources to the atmosphere are:

- Gasoline and diesel fuelled vehicles
- Forest fires
- Woodburning stoves and fireplaces

These three sources contribute approximately 97% of the estimated 260 MT/y of total PAH atmospheric emissions in Ontario. The remaining contributions are primarily from industrial operations (including coke manufacturing, coal-fired thermal generation stations and incinerators) and residential, commercial and institutional heating. The estiamted total PAH emission is believed to be uncertain by a factor of about two, because of data limitations.

The emission factors for PAH that are major contributors to the total PAH from these sources are summarized in Table ES-1. Phenanthrene and its methyl derivatives, pyrene, anthracene and its methyl derivatives and benzo[a]pyrene are the most ubiquitous based on the number of entries in the Table. On the other hand, benzo[k]fluoranthene is only recorded once; so too, are perylene, fluorene, dibenz[a]anthracene and its methyl derivatives and benzo[e]pyrene. Whereas, it was noted that benzo[k]fluoranthene was produced at a relatively high concentration in coke oven emissions, the information obtained during the study provided no guide regarding potential PAH source markers. Indeed, this review discoverd no recorded unambiguous procedure for identifying chemical markers that could be clearly attributed to a specific source.

The report also discusses sources and inputs to water and soil, and it is estimated that nearly 75% of the PAH loadings to soil and water arise from rainfall; the remaining inputs are from industrial discharges, including water pollution control plants, and there is also a significant contribution to water arising from urban run off (10-15%).

PAH that are most persistent and frequently detected at relatively high concentration in water include benz[a]anthracene, benzo[k]fluoranthene and pyrene in treated discharge from water treatment plants, based on an extensive study carried out on 37 high flow rate plants. Similarly, sludges produced from these facilities also showed higher levels of acenaphthylene, phenanthrene, and pyrene, compared to the other PAH detected.

TABLE ES-1

Summary Table of Emission Factors for Major PAH from Predominant Sources in Ontario

PAH	Coke Manufacturing(1) (mg/MT coal)	Coal-fired TGS(2) (mg/MT)	Incinerators(3) (mg/MT waste)	Residential Heating(4) (mg/GJ)	Forest Fires(5) (mg/MT)	Unleaded Gasoline Fuelled(6) Vehicles (mg/kL)	Diesel Fuelled Vehicles(7) (mg/kL)
A				395	6,760*		696
Acey			1,000				
B[k]F	31						
B[a]A		ND.-3			836		
B[e]P					152		
B[a]P	55	0.3-48			241		
B[a]FLN		0.7-4					2,335
B[ghi]Per	25	0.04-5.7			836		
B[c]Phen				105	175		
Chr		N.D.-5.5					
DB[a]A		N.D.-5					
DMBA		1.6-12					
F	100	N.D.-15.6	140	244	1,051**	27-115	1,860
FLN				308			
MeA		0.2-16.5		144	7,611		
MeP					2,450**		
MePhen		0.5-7		967		32-275	1,760
MeChr					1,559		
P		3.3-1		171	1,133		
Phen		0.03-31.5		644	*	52-220	2,600
Per	44						

(1) Canadian Emission factors for Battery Stacks
(2) Canadian Emission Factors greater than or equal to 3.0mg/MT coal.
(3) Emission Factors for municipal solid waste incinerators - greater than 100 mg/MT waste feed.
(4) Emission Factors for a conventional wood stove - greater than 100 mg/GJ.
(5) Emission Factors greater than 100 mg/MT.
(6) Emission Factors greater than 100 mg/kL.
(7) Emission Factors greater than 1,000 mg/kL.

* Includes A and Phen
** Contributions from F and MeP to both entries in the Table.

Based on the rainfall flux data, those PAH present at relatively high concentration compared to other PAH comprising the total are: phenanthrene, fluorene, benzo[b]fluorene, benzo[ghi]perylene and indeno[1,2,3,-cd]pyrene. Other studies indicate that pyrene and benzo[a]pyrene are probably the two PAH that constitute the greatest fraction of the total PAH loading to the Great Lakes.

It is inferred from the available data that PAH levels in soils vary widely, with urban soils containing from 100 to 1,000 ug/kg benzo[a]pyrene; the higher concentrations are associated with locations near highways, airports, rail stations, and heavy industry. Similarly, it was inferred that the levels of phenanthrene, fluoranthene, and pyrene were significantly higher in urban run off than other PAH.

Information collected from the literature search indicates that nitration and oxidation reactions occur with PAH, which alter the source PAH to a substituted or a ring-opened form. The kinetics of these reactions are influenced by light intensity, the size of the particle to which the PAH is adsorbed and temperature. Reactions are very much slower in the aqueous phase, partly because of the hydrophobic nature of these compounds. For example, it is estimated that the $t_{1/2}$ for bacterial oxidation of anthracene in water is about 15 days.

The particle-bound PAH detected in the ambient air show elevated levels of benzo[ghi]perylene in industrialized towns with high traffic densities, such as Hamilton, and much lower levels for towns with lower traffic densities such as Sudbury. As expected, these levels also show a strong seasonal dependence with significantly higher levels of PAH in the ambient air during the Fall (October-December) for most locations. Other studies show phenanthrene, fluoranthene, fluorene and its methyl derivatives and pyrene are, on average, the commonest PAH in the ambient air in Toronto.

An attempt was made to determine the exposure level for individuals resident in Ontario. It is estimated that the PAH exposure, other than occupational, is 1.5 - 2.1 mg/yr depending on whether the individual is a smoker or non-smoker. Estimates are summarized in Table ES-2.

The study clearly identifies certain major gaps in terms of available and, in many cases, reliable information on the sources and inputs of PAH and their fate in the Ontario environment.

Thermodynamic modelling (so-called fugacity modelling) was used to assess both the potential for partitioning of PAH into the various environmental media as well as the sensitivity of such a tool for predicting the uncertainty in values of the physical properties of PAH. This exercise identified that much better data on vapour pressures are needed to reduce the uncertainty of environmental fate modelling.

As an example of the kind of useful information produced by this modelling exercise, phenanthrene, which has a relatively high vapour pressure and thus might be expected to reside primarily as a vapour in the atmosphere, is predicted to be widely distributed among all environmental compartments. This prediction is consistent with actual measurements, which show phenanthrene to be ubiquitous in all media.

TABLE ES-2

Estimated Average PAH Exposure per Individual in Ontario

	PAH INTAKE (ug/yr)
Food	1299
Drinking Water	36.5
Inhalation	30
Indoors (non-smoking)	70
Indoors (smoking & fireplaces)	700
TOTAL PAH INTAKE	1.5 - 2.1 mg/yr.

One of the most important conclusions to be drawn from the review is that it would be beneficial for Canadian (and other) jurisdictions to agree on a standard minimum set of PAH to monitor in all environmental media, or compartments, regardless of whether a particular PAH is expected to be found in a particular medium. The reason for this suggestion is that only when the detailed distributions of selected PAH are known can it be concluded that their environmental transformations and fate are understood. Missing data for some media create significant uncertainty.

The data presented in the report suggest that it is not possible at present to track mixtures emitted or discharged from a given source unambiguously from source to receptors over any significant distance. Near sources of emissions or discharge, that is, within the first few kilometres, source profiles of PAH mixtures may allow direct source-receptor analysis. Further away from sources, environmental chemistry (especially atmospheric chemistry) and physical processes (especially atmospheric precipitation) alter the characteristics of PAH mixtures so that measurements at distant receptor sites contain ambiguous information about source origins. For this reason, the report suggests that air emission source assessment for regulatory source apportionment would best be concentrated on chemically stable, particle-bound PAH.

Human and environmental exposure estimates by means of measurements in the environment, depend of course, upon total PAH measurements, rather than just particle-bound PAH.

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TABLE OF CONTENTS

Page

Acknowledgement

Executive Summary i

1.0 INTRODUCTION 1-1

1.1 Background 1-1
1.2 Technical Program 1-2
1.3 Polycylic Aromatic Hydrocarbon (PAH) Priority List 1-3
1.4 Addenda 1-5

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS 2-1

2.1 Nomenclature and Structure 2-1
2.2 Chemical and Physical Properties 2-2
2.3 Chemical Reactivity 2-15
2.4 Summary 2-19

3.0 SOURCES AND INPUTS OF PAH TO THE ATMOSPHERE 3-1

3.1 Introduction 3-1
3.2 Sources and Inputs 3-1
3.3 Atomospheric/Terrestrial Sources and Input Data 3-5
3.3.1 Industrial Discharges 3-6
3.3.1.1 Coke Production 3-7
3.3.1.2 Metal Processing 3-15
3.3.1.3 Coal Liquefaction 3-15
3.3.1.4 Petroleum Refining (Catalytic Cracking) 3-17
3.3.1.5 Production of Pyrolysis Products (Coal Tar/ Creosote/Anthracene Oil/Coal Tar Pitch/ Carbon Black) 3-19
3.3.2 Power Production Sources 3-25
3.3.2.1 Coal Mining (Coal Dust) 3-25
3.3.2.2 Coal-Fired Power Plants 3-25
3.3.3 Municipal and Hazardous Waste Incinerators 3-31

TABLE OF CONTENTS (cont'd)

Page

3.3.4 Transportation 3-36
3.3.4.1 Gasoline and Diesel-Powered Vehicles 3-40
3.3.4.2 Tire Wear 3-44
3.3.4.3 Source Markers (Transportation) 3-44
3.3.5 Residential Heating 3-45
3.3.5.1 Emission Factors 3-45
3.3.5.2 Emissions (Oil and Gas Heating) 3-49
3.3.6 Open Burning of Biomasss 3-50
3.3.6.1 Burning of Treated Wood Waste 3-50
3.3.6.2 Forest Fires 3-52
3.3.6.3 Burning of Agricultural Waste 3-54
3.3.6.4 Source Markers 3-57
3.4 Summary of PAH Emissions to the Atomosphere 3-57

4.0 TERRESTRIAL AND AQUATIC SOURCES AND INPUTS

4.1 Wet/Dry Deposition from the Atomosphere 4-1
4.1.1 Plant Uptake 4-1
4.1.2 Biosynthesis 4-7
4.1.3 Diagenesis 4-7
4.1.4 Wood Preservation 4-9
4.1.5 Sewage Sludge Disposal 4-13
4.1.6 Disposal of Oil Refinery Sludges 4-20
4.1.7 Coal Gasification Wastes 4-22
4.2 Direct Deposition (Wet/Dry) from the Atmosphere to Aquatic Systems 4-24
4.2.1 Rainfall as a PAH Source 4-25
4.3 PAH Uptake in Soils near Industrial Operations 4-35
4.4 Municipal Effluents 4-38
4.5 Runoff 4-42
4.6 Oil Spills 4-46
4.6.1 Refinery Losses to Water 4-50
4.6.2 Gasoline and Diesel Oil Loss During Tank Refilling 4-50
4.6.3 Waste Oill from Transportation 4-50
4.6.4 Disposal of Dredging Spoils 4-52
4.7 Leachate from Waste Disposal Sites 4-52
4.8 Treated Wood Structures for Piers 4-52
4.9 Transboundary Movement of Polycyclic Aromatic Hydrocarbons 4-57
4.10 Summary of PAH Emissions to Soil and Water 4-60

TABLE OF CONTENTS (cont'd)

Page

5.0 ENVIRONMENTAL PROCESSES AND FATE OF PAH 5-1

5.1 Introduction (Air) 5-1
5.1.1 Chemical Reactivity (Atmospheric Aspects) 5-2
5.1.1.1 Particle Lifetime 5-3
5.1.1.2 Reactions with Nitrating Species 5-6
5.1.1.3 Reactions with Ozone 5-11
5.1.1.4 Reactions with Sulphur Oxides 5-13
5.1.1.5 Photolysis of PAH Compounds 5-15
5.1.1.6 Concentrations of Oxy- and Nitro-PAH in the Atmosphere 5-18
5.1.2 Long Range Transport of PAH 5-22
5.2 Soil 5-24
5.2.1 Degradation in Soils 5-25
5.2.2 Sorption 5-29
5.2.3 Volatilization 5-31
5.2.4 Photolysis 5-31
5.3 Water 5-32
5.3.1 Abiotic Processes 5-32
5.3.1.1 Solubility and Sorption 5-32
5.3.1.2 Volatilization 5-38
5.3.1.3 Photodegradation 5-42
5.3.2 Biological Processes 5-48
5.3.2.1 Bioavailability and Bioaccummulation 5-48
5.3.2.2 Biodegradation 5-60
5.3.4 Micocosm Studies 5-63

6.0 ENVIRONMENTAL LEVELS AND SOURCE CONTRIBUTIONS 6-1

6.1 Levels in Air, Soil and Water 6-1
6.2 Residue Levels in Ontario Soils 6-10
6.3 Residue Levels in Sediments 6-10
6.4 Residue Levels in Fish and Wildlife 6-13
6.5 PAH in Human Tissues and Fluids 6-21
6.6 Trends in Levels and Source Contributions 6-23

TABLE OF CONTENTS (cont'd)

Page

7.0 HUMAN EXPOSURE LEVELS (DIETARY AND LIFESTYLE SOURCES) 7-1

7.1 PAH in Ontario Food 7-2
7.1.1 Analysis of PAH in Foods 7-4
7.1.2 Total Diet Studies 7-10
7.1.3 Summary - PAH in Food Available in Ontario 7-11
7.2 PAH in Ontario Drinking Water 7-11
7.2.1 Summary 7-13
7.3 PAH in Pharmaceuticals, Cosmetics 7-14
7.3.1 Coal Tars 7-14
7.3.2 Soft and Liquid Paraffins, Mineral Oils 7-15
7.3.3 Summary 7-15
7.4 PAH in Indoor Air 7-16
7.4.1 Effects of Combustion Processes (for Heating) 7-16
7.4.2 Effects of Tobacco Smoke 7-18
7.4.3 Indoor PAH from Miscellaneous Sources 7-20
7.4.4 Summary 7-21
7.5 Estimated Levels of Human Exposures 7-21

8.0 ASSESSMENT OF ENTRY, MOBILITY AND FATE OF POLYCYCLIC AROMATIC HYDROCARBONS 8-1

8.1 Physical Partitioning and Chemical Transformation of PAH and PAH Mixtures 8-1
8.2 Modelling the Fate of PAH Compounds 8-4
8.3 Results and Discussion 8-9
8.4 Advanced Model Predictions 8-18
8.5 Emission Rate Estimates 8-25
8.5.1 Estimation of Ambient PAH Concentration for Hamilton 8-26
8.6 Estimate of the LRT Contribution to PAH Levels in Ontario 8-31
8.7 Regional Estimates for PAH Emissions in Ontario 8-35

9.0 REFERENCES 9-1

APPENDIX A - Level 3 Fugacity Model Data

APPENDIX B - Maps Illustrating PAH Regional Estimates

LIST OF TABLES

		Page
Table ES-1	Summary Table of Emission Factors for Major PAH from Predominant Sources in Ontario	iii
Table ES-2	Estimated Average PAH Exposure per Individual in Ontario	iv
Table 1-1	Polycyclic Aromatic Hydrocarbons in the Preliminary List by the Ministry of the Environment	1-4
Table 1-2	List of 47 PAH Species	1-6
Table 1-3	Polycyclic Aromatic Hydrocarbons on Revised Ministry of the Environment List That Were Not Assessed in This Study	1-7
Table 2-1	Chemical Structures of Priority Polycyclic Aromatic Compounds	2-4
Table 2-2	Summary Table of Selected Chemical and Physical Properties of Polycyclic Aromatic Hydrocarbons	2-13
Table 3-1	Estimated PAH Emissions	3-3
Table 3-2	Global Estimated Inputs of Benzo[a]Pyrene and Total PAH to the Aquatic Environment from Various Sources	3-4
Table 3-3	Emission Factors for Coke Production	3-8
Table 3-4	Emission Profiles and Factors for Coke Production	3-9
Table 3-5	Summary of PAH Emission Factors for Battery Stack Emissions During Coke Pushing Operations in Ontario	3-10
Table 3-6	Estimated Values for PAH, B[a]P and Particulate Matter During Total Coking Operations in Ontario	3-12
Table 3-7	Emission Factors for Foundries	3-16

LIST OF TABLES (cont'd)

		Page
Table 3-8	Mean Emission Factors for Fluid Bed Petroleum Cracking Catalyst Regenerators (controlled versus uncontrolled)	3-18
Table 3-9	PAH Concentration Range in the Plume from the Three Refineries Located in Montreal	3-20
Table 3-10	Average PAH Emission Factors and Total PAH Loading for Fluid Bed (FCC) Catalyst Regenerating Units for Petroleum Refineries	3-21
Table 3-11	PAH Emission Rates from a Coal Tar Distillation Plant in Hamilton	3-22
Table 3-12	PAH Emission Factors from an Oil- Furnace Carbon Black Plant	3-24
Table 3-13	Average PAH Emission Factors for Differently-Fired Coal Power Plants	3-27
Table 3-14	PAH Emission Factors for Coal-Fired Thermal Generating Stations	3-28
Table 3-15	Ontario Hydro Lambton and Nanticoke Thermal Generating Stations Emission Rates of Polycyclic Aromatic Hydrocarbons	3-29
Table 3-16	Estimated PAH, B[a]P and Total Suspended Particulate (TSP) Emissions for Ontario Hydro's Coal-Fired Power Generating Statins	3-30
Table 3-17	PAH Emission Data for TRICIL Hazardous Waste Incinerator	3-32
Table 3-18	NITEP PAH Emission Data and Levels in Incinerator Ash	3-34
Table 3-19	Group Test Averages for Stack Sampling Results	3-35
Table 3-20	Summary Table of PAH Emission Factors from MSW Industrial Liquid Waste and Commercial Incinerators	3-37
Table 3-21	Estimated Annual PAH Atmospheric Emissions to the Ontario Environment from Incinerators	3-38

LIST OF TABLES (cont'd)

		Page
Table 3-22	Polycyclic Aromatic Hydrocarbons Detected on Gasoline and Diesel Exhaust Particles	3-41
Table 3-23	Emission Factors for Gasoline and Diesel Powered Mobile Sources	3-42
Table 3-24	Estimates of Yearly PAH Emissions from Transportation Sources in Ontario	3-43
Table 3-25	Typical Emission Factors for Residential Heating	3-47
Table 3-26	Emission Profiles and Factors for PAH from Different Fuels in a Conventional Wood Stove	3-48
Table 3-27	Derived Emission Factors for the Burning of Creosote Treated Railway Ties	3-51
Table 3-28	Emission Factors of Polycyclic Aromatic Compounds for Burning Pine Needles	3-53
Table 3-29	Wildfire and Prescribed Burn Occurrence in Ontario, 1984 to 1988	3-55
Table 3-30	Average Yearly Emission Data for Polycyclic Aromatic Hydrocarbons from Wild and Prescribed Forest Fires in Ontario	3-56
Table 3-31	Summary Table - Atmospheric PAH Emissions	3-58
Table 4-1	Mean PAH Concentrations (mg/MT fresh weight) in Lettuce Grown at Various Distances from a Highway	4-3
Table 4-2	Mean PAH Concentrations (mg/MT fresh weight) in Whole Rye Grains Grown at Various Distances from a Highway	4-4
Table 4-3	Regression Equations for Plant Uptake of Polynuclear Aromatic Hydrocarbons	4-6
Table 4-4	PAH Content of Creosote, Creosote Sludge and Coal Tar	4-10
Table 4-5	Northern Wood Perservers Survey Soil and Sediment	4-11

LIST OF TABLES (cont'd)

		Page
Table 4-6	Northern Wood Perservers Survey Groundwater	4-12
Table 4-7	Summary of MISA PAH Data for 37 Ontario Water Pollution Control Plants	4-14
Table 4-8	Summary of Ontario Water Pollution Control Plants Tested, Flow Rates, PAH Concentrations and Estimated PAH Emission Rates	4-15
Table 4-9	Loadings of PAH to the Hamilton Sewage Treatment Plant in Raw Sewage and from the Plant in Treated Effluent	4-18
Table 4-10	Summary of Canadian and Internation Data on PAH in Municipal Sewage Sludge	4-19
Table 4-11	Concentrations of Base-Neutral Organics in Oil Refinery Disposal Sludges	4-23
Table 4-12	Data for the Correlation Between PAH Deposited and the Amount of Rain	4-27
Table 4-13	Particle-Bound and Dissolved PAH Concentrations in Rainfall Collected in a Residential Area of Portland, Oregon	4-28
Table 4-14	Annual Rates of Total Deposition of PAH in Forest Ecosystems	4-29
Table 4-15	Total Deposition of PAH to the Great Lakes	4-31
Table 4-16	PAH Fluxes to Sediments from 5 Remote Sites in the Northeastern United States and 3 Urban Sites	4-32
Table 4-17	PAH-Rainwater Concentration Data	4-34
Table 4-18	Concentrations of Polycyclic Aromatic Hydrocarbons in Soil Collected at Different Sites from the Algoma Steel: Sault Ste. Marie Plant	4-36
Table 4-19	Ratios of the Concentrations of PAH to Benzo[e]Pyrene in Soil Near Roadways	4-37
Table 4-20	Concentrations of PAH in Surface Soil at Different Sites in the Vicinity of Birmingham, U.K.	4-39

LIST OF TABLES (cont'd)

		Page
Table 4-21	Average Concentrations of PAH Discharged from the Hamilton WPCP	4-40
Table 4-22	Estimated Output of PAH for Hamilton Waste Treatment Plant	4-41
Table 4-23	Concentration of PAH in Palos Verdes Shelf and Santa Monica Bay Sediments	4-43
Table 4-24	Best Estimates of Mean Concentrations of Polyaromatic Hydrocarbons in Urban Runoff	4-44
Table 4-25	Annual Loadings of Polyaromatic Hydrocarbons in Urban Runoff in the Great Lakes Basin	4-45
Table 4-26	New York Storm Sewer Sediment Analysis	4-47
Table 4-27	Total Loadings of PAH to Niagara River in Runoff	4-48
Table 4-28	Polycyclic Aromatic Hydrocarbons in Used Motor Oil	4-49
Table 4-29	Estimated PAH Losses from Ontario Refineries in Wastewater	4-51
Table 4-30	Organic Compounds Identified in Extracts of Runoffs from Different Coals	4-53
Table 4-31	Estimated Yearly Volumes of Coal Pile Runoff and Leachate at Coal-Fired Generated Stations in Ontario	4-55
Table 4-32	Estimated PAH Loadings from Ontario Generation Stations Coal Pile Runoff	4-56
Table 4-33	Loadings of PAH to the Niagara River	4-58
Table 4-34	Annual Total Loadings of PAH in Water and Sediment in Urban Runoff for the Niagara River	4-59
Table 4-35	Input of Particulate-Associated Contaminants to Western Lake Superior from the St. Louis River and Duluth Harbor Area	4-61

LIST OF TABLES (cont'd)

		Page
Table 4-36	PAH Emission Profile from 24 Point Source Discharges to the St. Clair River	4-62
Table 4-37	Estimated PAH Loadings to the Soil and Water	4-63
Table 5-1	Summary of Photolytic and Electrophilic	5-4
Table 5-2	Classification of PAH Based on Electrophilic Nitration Reactions	5-8
Table 5-3	Outdoor Chamber Studies of PAH Reactions with O_3, NO_2, and hv[1]	5-14
Table 5-4	Half-Lives (in Hours) for the Photolysis of PAH on Different Substrates Determined in the Rotary Photoreactor	5-19
Table 5-5	Ambient Concentrations of Selected Nitro-PAH	5-21
Table 5-6	A Comparison Half-Lives Calcualted on the Basis of First or Zero Order Models from Data Colelcted by Bulman et al. (1985)	5-28
Table 5-7	PAH in Subsurface Water Samples (ng/L) of the Detroit River	5-35
Table 5-8	PAH in Suspended Solids (ng/g, dry weight) of the Detroit River	5-36
Table 5-9	PAH in Surficial Sediment Samples (ng/g, dry weight) of the Detroit River	5-37
Table 5-10	Mean PAH Concentrations Measured in Lake Michigan Sediment, Pore Water, Dissolved and Particulate Paired Samples	5-39
Table 5-11	Free-Radical Oxidation of Some PAH in Air-Saturated Water	5-43
Table 5-12	Photodegradation of PAH Under Natural Light in Mixed Acetone-Water or Carbon Tetrachloride-Water Solutions	5-44
Table 5-13	Photo-oxidation of Some Dissolved PAH Under Natural Sunlight Conditions	5-45

LIST OF TABLES (cont'd)

		Page
Table 5-14	Direct Photolysis of PAH in a 5 Metre-Deep Inland Water Body	5-47
Table 5-15	Range of Polycyclic Aromatic Hydrocarbon Concentrations	5-49
Table 5-16	Average Polycyclic Aromatic Hydrocarbon Concentrations	5-50
Table 5-17	PAH Bioconcentration Factors (BCF) for Selected Species of Aquatic Organisms	5-54
Table 5-18	Observed Versus Predicted Bioconcentration Factors for Selected PAH	5-59
Table 5-19	Degradation Rate Constants (k) and Half-Lives for Mixed Bacterial Populations in Water and Sediment from the Sme Stream	5-62
Table 6-1	Mean Ambient Air Levels of Polycyclic Aromatic Hydrocarbons at Niagara-on-the-Lake	6-3
Table 6-2	Mean Ambient Air Levels of Polycyclic Aromatic Hydrocarbons Near Niagara-on-the-Lake	6-4
Table 6-3	Particle-Bound PAH Concentration Ranges in Ambient Air Measurements for 4 Ontario Cities	6-6
Table 6-4	Total Particle-Bound Concentrations of 10 PAH in the Ambient Air of 4 Ontario Cities	6-7
Table 6-5	Summary of Mean Total PAH Concentration	6-8
Table 6-6	PAH Concentrations in Surface Watter	6-11
Table 6-7	PAH Data for Erie, PA	6-12
Table 6-8	PAH Concentration in Suspended Sediments	6-14
Table 6-9	Polynuclear Aromatic Hydrocarbons in Hamilton Harbour Sediments	6-15
Table 6-10	Mean, Minimum and Maximum Values of PAH	6-16

LIST OF TABLES (cont'd)

		Page
Table 6-11	PAH in St. Lawrence River Sediments Samples	6-17
Table 6-12	Abundances of Polycyclic Aromatics in Lake Ontario Sediment	6-18
Table 6-13	Highest PAH Values Recorded in Fish Collected from the Great Lakes	6-19
Table 6-14	Polynuclear Aromatic Hydrocarbons in Great Lakes Fish	6-20
Table 6-15	Identification of Polynuclear Aromatic Hydrocarbons in Great Lakes Herring Gull Lipid	6-22
Table 7-1	Summary of PAH Levels in Foods Available in Ontario	7-12
Table 7-2	Estimated Average PAH Exposures per Individual in Ontario	7-23
Table 8-1	Volumes of Environmental Segments	8-8
Table 8-2	Results for Level One Analysis of PAH Data	8-10
Table 8-3	Distribution of PAH into Air, Water and Organic Components Based on Raw Property Data	8-11
Table 8-4	Sensitivity Analysis of Input Data for Level One Analysis	8-13
Table 8-5	Distribution Changes Due to Vapour Pressure Sensitivity	8-14
Table 8-6	Distribution Changes Due to Water Solubility Sensitivity	8-15
Table 8-7	Distribution Changes Due to K_{ow} Sensitivity	8-16
Table 8-8	Point Source Emission Inventory for Hamilton	8-28
Table 8-9	Summary of Modelling Results ISCLT Model Predictions for 1979 and 1984 for the Hamilton Area	8-30
Table 8-10	Percentage Contribution to TSP from Coke Ovens, Traffic and Other Sources in Hamilton	8-32

LIST OF FIGURES

		Page
Figure 2-1	IUPAC Nomenclature, Lettering and Labelling for Pyrene and Benzo(a)Pyrene	2-3
Figure 5-1	Sediment Concentrations of Individual PAH in Lake Erie	5-40
Figure 5-2	PAH Concentration (log scale)	5-41
Figure 6-1	Graphical Illustration of Benzo[a]Pyrene Concentration and Year of Study at Chippewa/ Niagara Falls	6-5
Figure 8-1	Level III Fugacity Model Results for B[a]P in Ontario	8-22

1.0 INTRODUCTION

1.1 Background

The Ontario Ministry of the Environment is currently examining a number of priority chemicals with the intent of setting multi-media standards for their emission or discharge into the environment. This work is being undertaken by the Standards Development and Coordination Section of the Ministry's Hazardous Contaminants Coordination Branch and has already led to the publication of a scientific criteria document on polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (MOE, 1985). Currently, work is underway to prepare a similar document on polycyclic aromatic hydrocarbons (PAH), and the information base is being developed under the following headings:

- Environmental Characteristics: Properties, Sources, Levels and Fate;
- Environmental Toxicology; and
- Human Toxicology.

1.2 Technical Program

The overall objective of this project is to prepare a comprehensive background report on the physical and chemical properties of polycyclic aromatic hydrocarbons (PAH); their sources, uses, input and fate in the Ontario environment and levels in air, water, soil, sediments, sludge and food in Ontario.

The scope of the project is designed to achieve the following goals:

1. to review the nomenclature, structure, physical and chemical properties for a minimum of thirty-four environmentally or biologically important PAH of particular interest to the Hazardous Contaminants Coordination Branch (HCCB) of the Ontario Ministry of the Environment. PAH such as naphthalenes and quinones were not to be included.

2. to determine the composition and concentrations of PAH in the environment as single compound species and/or as environmental profile mixtures. Sources and inputs were to be addressed in the report.

3. to estimate the ambient levels and quantities of PAH in Ontario air, water, fish, other aquatic life, vegetation, soil, sediments, food and mining, smelting, municipal and industrial water, where possible, for comparison with levels found elsewhere in Canada and other countries.

   The primary goal under this heading was the determination or estimation of a PAH mass balance (budget) for Ontario using the data collected from items 1-3 above.

4. to estimate the average PAH exposure levels of humans in Ontario based on the ambient levels and modifiers arising from specific dietary and lifestyle sources.

5. to estimate the trend in environmental levels as a means of predicting future PAH levels in Ontario.

1.3 Polycyclic Aromatic Hydrocarbon (PAH) Priority List

A list of thirty-four priority polycyclic aromatic hydrocarbons (PAH) was proposed by the Hazardous Contaminants Coordination Branch (HCCB) for assessment (Table 1-1). Selection was based on the following criteria:

- where the quantity of a selected PAH generated or emitted into the environment was believed to be significant;
- where a selected PAH was suspected to have adverse health effects; and
- where a selected PAH might serve as a source marker.

In the course of this work, several additional PAH were considered for inclusion in the final list. Compounds were selected on the basis of the following criteria.

- use as a potential source marker;
- inclusion in the Ministry of the Environment Municipal/Industrial Strategy for Abatement (MISA) Effluent Monitoring Priority Pollutants List (EMPPL);
- their occurrence in soil samples in Ontario;
- toxicity; and
- their occurrence in source profiles of what are believed to be the five (5) largest contributors of PAH to the Ontario environment, viz: forest fires, residential wood and oil heating, mobile sources, oil-fired boilers and coke ovens (OME, 1979).

TABLE 1-1

Polycyclic Aromatic Hydrocarbons in the Preliminary List by the Ministry of the Environment

1 Acenaphthene
2 Acenaphthylene
3 Anthanthrene
4 Anthracene
5 Benzo[a]fluorene
6 Benzo[a]pyrene
7 Benzo[b]fluoranthene
8 Benzo[e]pyrene
9 Benzo[ghi]perylene
10 Benzo[j]fluoranthene
11 Benzo[k]fluoranthene
12 Benz[a]anthracene
13 Carbazole
14 Chrysene
15 Coronene
16 Cyclopenta[cd]pyrene
17 Dibenzothiophene
18 Dibenzo[c,g]carbazole
19 Dibenz[a,h]acridine
20 Dibenz[a,h]anthracene
21 Dibenz[a,j]acridine
22 Dinitropyrene[1,6-]
23 Dinitropyrene[1,8-]
24 Fluoranthene
25 Fluorene
26 Indeno[1,2,3-cd]pyrene
27 Methylanthracenes
28 Methylphenanthrene[1-]
29 Nitrofluoranthene
30 Nitropyrene[1-]
31 Perylene
32 Phenanthrene
33 Pyrene
34 Triphenylene

The list developed by using these criteria and subsequently used by CONCORD for this report is presented in Table 1-2. This list includes the 34 PAH identified by the Ministry of the Environment as well as an additional 13 PAH that are believed to meet the required criteria.

1.4 Addenda

Subsequent to compiling the list of forty-seven (47) priority polycyclic aromatic hydrocarbons, a revised list of fifty-six (56) compounds was proposed by the Hazardous Contaminants Coordination Branch. Additional compounds in this list that were not examined in this project because of time and budgetary constraints are presented in Table 1-3.

They include amine- and hydroxy-substituted polycyclic aromatic hydrocarbons and relatively complex heterocyclic compounds such as benzo[b]naptho[2,1-d]thiophene.

TABLE 1-2

List of 47 PAH Species

1 Acenaphthene*
2 Acenaphthylene*
3 Anthanthrene*
4 Anthracene*
5 Benzo[a]Fluorene*
6 Benzo[a]Pyrene*
7 Benzo[b]Fluoranthene*
8 Benzo[b]Fluorene
9 Benzo[c]Chrysene
10 Benzo[c]Fluorene
11 Benzo[c]Phenanthrene
12 Benzo[e]Pyrene*
13 Benzo[ghi]Fluoranthene
14 Benzo[ghi]Perylene*
15 Benzo[g]Chrysene
16 Benzo[j]Fluoranthene*
17 Benzo[k]Fluoranthene*
18 Benz[a]Acridine
19 Benz[a]Anthracene*
20 Benz[c]Acridine
21 Acridine
22 Carbazole*
23 Chrysene*
24 Coronene*
25 Cyclopenta[cd]Pyrene*
26 Dibenzothiophene*
27 Dibenzo[a,e]Fluoranthene
28 Dibenzo[a,e]Pyrene
29 Dibenzo[a,h]Pyrene
30 Dibenzo[a,i]Pyrene
31 Dibenzo[a,l]Pyrene
32 Dibenzo[c,g]Carbazole*
33 Dibenz[a,c]Anthracene
34 Dibenz[a,h]Acridine*
35 Dibenz[a,h]Anthracene*
36 Dibenz[a,j]Acridine*
37 Dibenz[a,j]Anthracene
38 Dimethylphenanthrene[1,4-]
39 Dinitropyrene[1,6-]*
40 Dinitropyrene[1,8-]*
41 Fluoranthene*
42 Fluorene*
43 Indeno[1,2,3-cd]Pyrene*
44 Methylanthracenes*
45 Methylchrysene[1-]
46 Methylchrysene[2-,3-,4- and 6-]
47 Methylchrysene[5-]
48 Methylfluorene[2-]
49 Methylfluoranthene[2-]
50 Methylfluoranthene[3-]
51 Methylphenanthrene[1-]*
52 Naphtho[2,3-b]Pyrene
53 Nitroanthracene[9-]
54 Nitrobenzo[a]Pyrene[6-]
55 Nitrochrysene[6-]
56 Nitrofluoranthene*
57 Nitropyrene[1-]*
58 Perylene*
59 Phenanthrene*
60 Pyrene*
61 Tribenzo[aei]Pyrene
62 Triphenylene*
63 Dimethylbenzanthracene+
64 Nitro-Acenaphthene[5-]
65 Quinoline**

* Ministry of the Environment List
+ Presence in Refinery Waste Identified by the MOE
** Identified for Cigarette Smoke (alternative to nicotine)

TABLE 1-3

Polycyclic Aromatic Hydrocarbons on Revised Ministry of the Environment List That Were Not Assessed in This Study

Methylbenzanthracene

Dibenz[c,h]acridine (other isomers were included in primary list)

Nitrophenanthrenes

Benzo[b]naphtho[2,1-d]-thiophene

Benzo[2,3]phenanthro[4,5]-thiophene

Phenanthro[4,5-bcd]-thiophene

Aminofluoranthene

Aminophenanthrene

Aminopyrene

2-hydroxy benzo[a]pyrene

Hydroxynitro PAH

2.0 PHYSICAL AND CHEMICAL PROPERTIES OF POLYCYCLIC AROMATIC HYDROCARBONS

2.1 Nomenclature and Structure

The polycyclic aromatic hydrocarbons (PAH) referred to in this report are characterized by three or more fused benzene rings. In addition, compounds with this basic structure but having 5-membered rings, such as fluorene, and heterocyclic rings containing aza- or thio-arene substituents such as acridine and thiophene, are also included under this heading. In view of the basic symmetry of these compounds, several structural isomers are possible. The nomenclature proposed by the International Union of Pure and Applied Chemistry (IUPAC) is generally used for identification of these PAH, particularly for distinguishing between isomers and ring substituents. The following rules help determine the orientation for assigning ring numbering or lettering:

1. the maximum number of rings lie in a horizontal row;

2. as many rings as possible are above and to the far right of the horizontal row; and

3. if more than one orientation meets these requirements, the one with the minimum number of rings at the lower left is chosen.

In addition to these rules, numbering of carbons in the ring structure is carried out in a clockwise fashion, starting with the first carbon that is not part of another ring or part of ring fusion, which is located on the upper right. Letters are assigned in alphabetical order to ring faces and the face between carbons 1 and 2 is labelled "a", continuing clockwise around the molecule. This procedure is illustrated in Figure 2-1 for pyrene and benzo[a]pyrene.

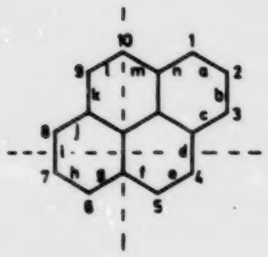
Structures for the forty-seven (47) PAH used in this evaluation are summarized in Table 2-1.

2.2 Chemical and Physical Properties

The chemical and physical properties of the forty-seven (47) compounds are presented in Table 2-2. Environmentally significant properties such as the boiling point, vapour pressure, solubility, octanol/water partition coefficient were compiled from sources such as the IARC monographs, 1983, 1984, 1985; CRC Handbook of Physics and Chemistry, 1987; HSDB, 1987; Lane, 1988 and EPS-Ontario, 1985.

FIGURE 2-1

IUPAC Nomenclature, Lettering and Labelling for Pyrene and Benzo[a]Pyrene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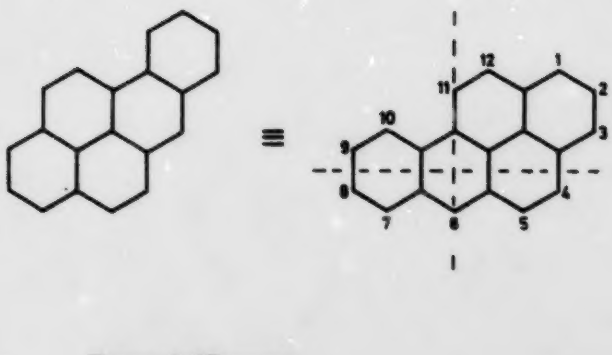
2 rings above and to the right of horizontal row.

Pyrene


≡
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12

Benzo[a]Pyrene

TABLE 2-1

Chemical Structures of Priority Polycyclic Aromatic Compounds

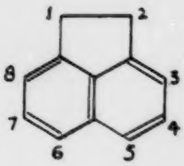
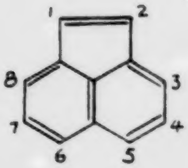
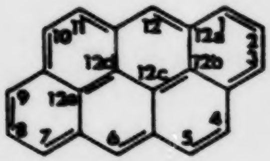
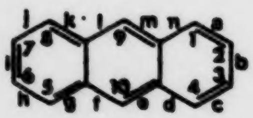
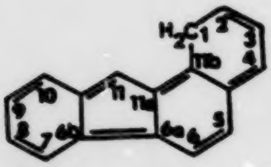
Structure	Name	Identification CAS #	Mol. Formula
	Acenaphthene	83-32-9	$C_{12}H_{10}$
	Acenaphthylene	208-96-8	$C_{12}H_8$
	Anthanthrene or Dibenzo[def,mno] chrysene (IUPAC)	191-26-4	$C_{22}H_{12}$
	Anthracene (IUPAC)	120-12-7	$C_{14}H_{10}$
	Benzo[a]fluorene (IUPAC)	238-84-6	$C_{17}H_{12}$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

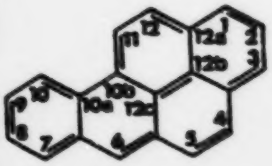
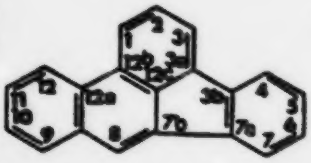
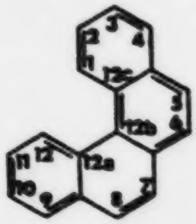
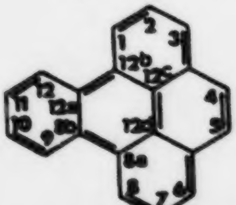
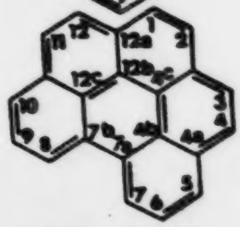
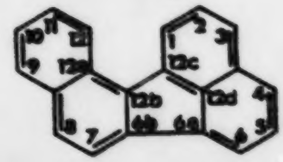
Structure	Name	Identification CAS #	Mol. Formula
	Benzo[a]pyrene (IUPAC)	50-32-8	$C_{20}H_{12}$
	Benzo[b]fluoranthene	205-99-2	$C_{20}H_{12}$
	Benzo[c]phenanthrene	195-19-7	$C_{17}H_{12}$
	Benzo[e]pyrene	192-97-2	$C_{20}H_{12}$
	Benzo[ghi]perylene	191-24-2	$C_{21}H_{12}$
	Benzo[j]fluoranthene	205-82-3	$C_{20}H_2$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

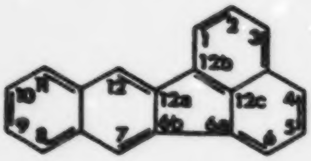
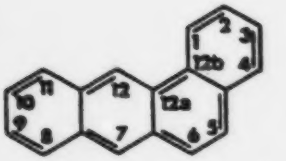
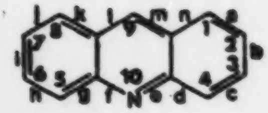
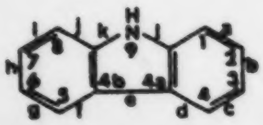
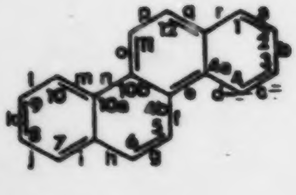
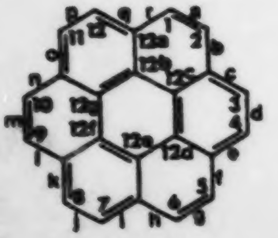
Structure	Name	Identification CAS #	Mol. Formula
	Benzo[k]fluoranthene	207-08-9	$C_{20}H_{12}$
	Benz[a]anthracene	56-55-3	$C_{18}H_{12}$
	Acridine	260-94-6	$C_{13}H_9N$
	Carbazole	86-74-8	$C_{12}H_9N$
	Chrysene	218-01-9	$C_{18}H_{12}$
	Coronene	191-07-1	$C_{24}H_{12}$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

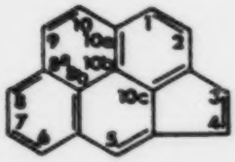
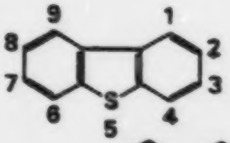
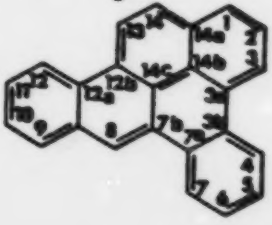
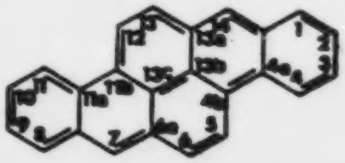
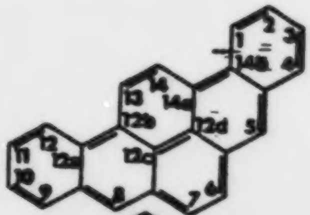
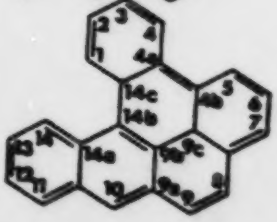
Structure	Name	Identification CAS #	Mol. Formula
	Cyclopenta[cd] pyrene	27208-37-3	$C_{18}H_{10}$
	Dibenzothiophene	132-65-0	$C_{12}H_8S$
	Dibenzo[a,e]pyrene	192-65-4	$C_{24}H_{14}$
	Dibenzo[a,h]pyrene	189-64-0	$C_{24}H_{14}$
	Dibenzo[a,i]pyrene	189-55-9	$C_{24}H_{14}$
	Dibenzo[a,l]pyrene	191-30-0	$C_{24}H_{14}$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

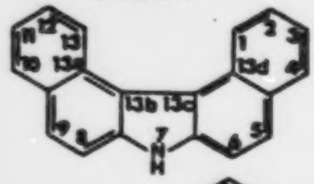
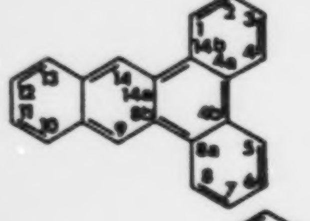
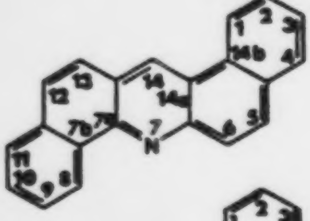
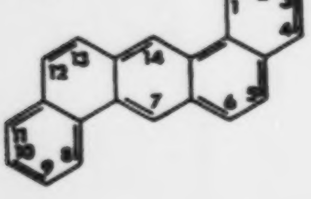
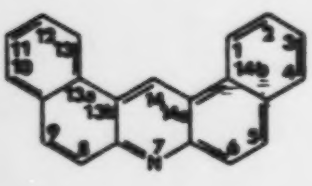
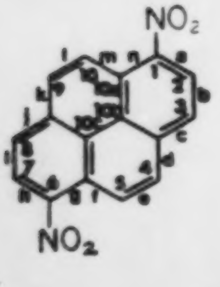
Structure	Name	Identification CAS #	Mol. Formula
	Dibenzo[c,g]carbazole	194-59-2	$C_{20}H_{13}N$
	Dibenz[a,c]anthracene	215-58-7	$C_{22}H_{14}$
	Dibenz[a,h]acridine	226-36-8	$C_{21}H_{12}N$
	Dibenz[a,h]anthracene	53-70-3	$C_{22}H_{14}$
	Dibenz[a,j]acridine	224-42-0	$C_{21}H_{12}N$
	Dinitropyrene[1,6-]	42397-64-8	$C_{16}H_{8}N_{2}O_{4}$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

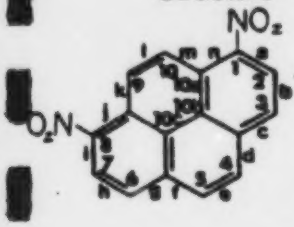
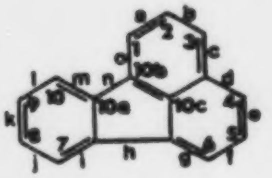
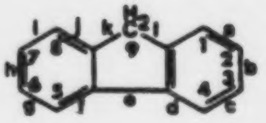
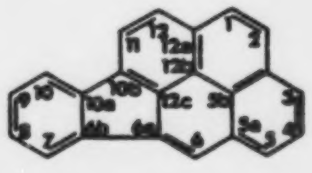
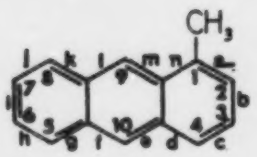
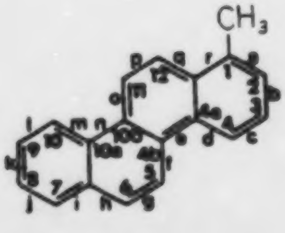
Structure	Name	Identification CAS #	Mol. Formula
	Dinitropyrene[1,8-]	42397-65-9	$C_{16}H_8N_2O_4$
	Fluoranthene	206-44-0	$C_{16}H_{10}$
	Fluorene	86-73-7	$C_{13}H_{10}$
	Indeno[1,2,3-cd] pyrene	193-39-5	$C_{22}H_{12}$
	Methylanthracenes (CAS # and structure for 1-methylanthracene is shown)	618-48-0	$C_{15}H_{12}$
	Methylchrysene[1-]	3351-28-8	$C_{19}H_{14}$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

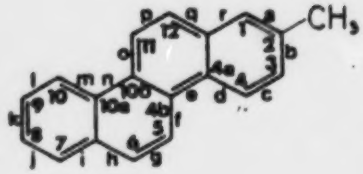
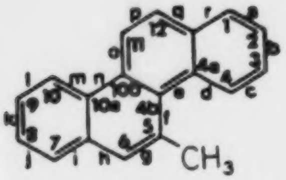
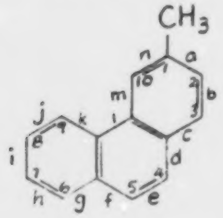
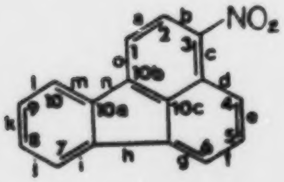
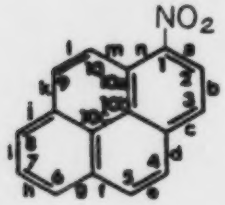
Structure	Name	Identification CAS #	Mol. Formula
	Methylchrysene[2-, 3-, 4-and 6-] (CAS # and structure for 2-Methylanthracene is shown here)	3351-32-4	$C_{19}H_{14}$
	5-Methylchrysene	3697-24-3	$C_{19}H_{14}$
	1-Methylphenanthrene	832-69-9	$C_{15}H_{12}$
	3-Nitrofluoranthene	892-21-7	$C_{16}H_9NO_2$
	1-Nitropyrene	5522-43-0	$C_{16}H_9NO_2$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

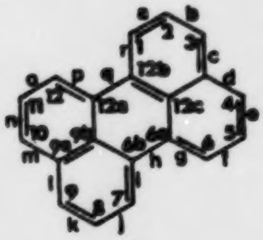
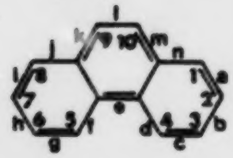
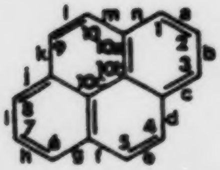
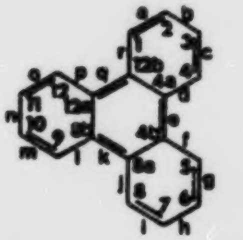
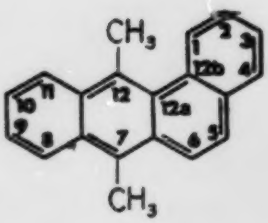
Structure	Name	Identification CAS #	Mol. Formula
	Perylene	198-55-0	$C_{20}H_{12}$
	Phenanthrene	85-01-8	$C_{14}H_{10}$
	Pyrene	129-00-0	$C_{16}H_{10}$
	Triphenylene	217-59-6	$C_{18}H_{12}$
	Dimethylbenz-anthracene (CAS # and structure for 7,12-Dimethylbenz[a]-anthracene is shown here)	57-97-6	$C_{20}H_{16}$

TABLE 2-1 (cont'd)

Chemical Structures of Priority Polycyclic Aromatic Compounds

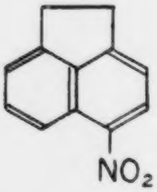
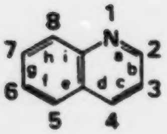
Structure	Name	Identification CAS #	Mol. Formula
	5-Nitro-acenaphthene	602-87-9	$C_{12}H_9NO_2$
 1 2 3 4 5 6 7 8 N a b c d e f g h i	Quinoline	91-22-5	C_9H_7N

TABLE 2-2

Summary Table of Selected Chemical and Physical Properties
of Polycyclic Aromatic Hydrocarbons

Compound	Abbrev.	M.W.	M.Pt. Range	M.Pt. Typical	log Kow	Henry's const. (kPa/gmole)	vap. pres. (kPa)	density (g/mL)	B.Pt.(°C) Range	B.Pt.(°C) Typ.	Sol. (water) (ppm)	Sol. (solvent) (g/ML)
Acenaphthene	ACE	154.2	93-97	96	4.03-4.15	24	2.9E-04-6.0E-04	1.22 (20°C)	277-280.7	278	2.42-7.37	
Acenaphthylene	ACEY	152.2	88-93	92	4.07	10.2	0.0001-0.0001c	0.885 (15°C)	156-176.5		3.93-6.0	n.a.
Acridine	ACR	179.2	108-110.5		3.4*	n.a.	0.13 @ 129.4°	1.1		346	100	n.a.
Anthanthrene	ANTHN	276.3		264	7.3*	n.a.	n.a.	n.a.		547*	0.056-0.077	n.a.
Anthracene	A	178.2	215-219	218	4.45*	45	0.13 (sublimes)	1.25	340-342	342	0.053	0.015##
Benzo[a]pyrene	B[a]P	252.3	176.5-179	179	6.0-6.5*	n.a.	6.7E-09-7.3E-9	1.35	495-496		0.004	n.a.
Benzo[a]fluorene	B[a]FLN	216.2	189.5-191	190	5.32-5.75	n.a.	n.a.	n.a.	390-413	413	0.045	n.a.
Benzo[b]fluoranthene	B[b]F	252.3	167-168.3	168	6.4-6.57*	n.a.	1.3E12-1.3E-07	n.a.	481-481.2		0.0015	n.a.
Benzo[c]phenanthrene	B[c]PHEN	228.3	66-68	68	5.65*	n.a.	n.a.	n.a.		427*	0.75-1.33	n.a.
Benzo[e]pyrene	B[e]P	252.3	178-179	178.7	5.98-6.4*	n.a.	7.3E-10	n.a.	492-493		0.0064(ave.)	n.a.
Benzo[ghi]perylene	B[ghi]PER	276.3	222-278.5	278.3	6.77-7.1	0.041	1.9E-14-1.3E-11	n.a.	500-503		0.00045(ave.)	n.a.
Benzo[j]fluoranthene	B[j]F	252.3		166	6.84*	n.a.	n.a.	n.a.		480	0.0025	n.a.
Benzo[k]fluoranthene	B[k]F	252.3	215.7-217		6.84*	n.a.	1.3E-11-13E-10	n.a.		480	0.00076	n.a.
Benz[a]anthracene	B[a]A	228.3	155-157		5.91	7.1E-08*	1.9E-11-3.7E-11	n.a.	400-437.8**		0.009-0.75*	n.a.
Carbazole	CARB	167.2	245-248		3.29-3.51	n.a.	1.9E-05*	1.1		355	93*	n.a.
Chrysene	CHR	228.3	255-256		5.6-5.9	n.a.	4.7E-12-7.7E-07	1.274 (20°C)		488	0.0018-0.0022	0.00077##(0.0021)$
Coronene	COR	300.4		439	6.0-10.3*	4.0E-08*	2.5E-16-2.0E-13	1.38 (20°C)		525	0.00014	n.a.
Cyclopenta[c]pyrene	CP[cd]P	226	171-175		5.47*	n.a.	n.a.	n.a.		548*	0.75-1.9*	n.a.
Dibenzothiophene	DBTHP	184.3	99-100		4.53*	n.a.	n.a.	n.a.	332-333		10.4*	n.a.
Dibenzo[a,e]pyrene	DB[a,e]P	302.4	233-234		7.22*	n.a.	n.a.	n.a.			0.027-0.073*	n.a.
Dibenzo[a,h]pyrene	DB[a,h]P	302.4		300	7.22*	n.a.	n.a.	n.a.			0.027-0.073*	n.a.
Dibenzo[a,i]pyrene	DB[a,i]P	302.4		280	7.22*	n.a.	n.a.	n.a.		275	0.027-0.073*	2000a; 5000b
Dibenzo[a,l]pyrene	DB[a,l]P	302.4	162-164		7.22*	n.a.	n.a.	n.a.			0.027-0.073*	2000a; 5000b
Dibenzo[c,g]carbazole	DB[c,g]CARB	267.3		158	5.72*	n.a.	n.a.	n.a.		566*	1.35*	n.a.
Dibenz[a,c]anthracene	DB[a,c]A	278.4		205	7.0-8.4*	8.5E-07*	1.9E-15-1.9E-08	n.a.	518-538		0.0005	n.a.
Dibenz[a,h]acridine	DB[a,h]ACR	279.4		226	5.63*	n.a.	n.a.	n.a.		524	1.7*	n.a.
Dibenz[a,h]anthracene	DB[a,h]A	278.4	266-270	266	6.0-7.0*	n.a.	1.3E-11	1.282	524-535		0.0005	n.a.
Dibenz[a,j]acridine	DB[a,j]ACR	279.4		216	n.a.	n.a.	n.a.	n.a.			1.6*	n.a.
Dimethylbenzanthracene	DMBA	256.4			7.33*	n.a.	n.a.	n.a.			0.024-0.025*	n.a.
Dinitropyrene[1,6-]	1,6-DNP	292.1	309-310		4.51*	n.a.	n.a.	n.a.			17.2*	n.a.
Dinitropyrene[1,8-]	1,8-DNP	292.1	299-300		4.51*	n.a.	n.a.	n.a.			17.2*	n.a.
Fluoranthene	F	202.3		111	5.22-5.28	0.38-0.53 (282°C)	1.2E-06-1.8E-03	1.25 (20°C)		383	0.24-0.26	n.a.
Fluorene	FLN	166.2	116-117		3.9-4.3	1.87-2.93 (282°C)	8.0E-05-1.3E-03	1.2		295	1.68-1.98	n.a.
Indeno[1,2,3-cd]pyrene	IN[123-cd]P	276.3	162.5-164	164	6.64-7.66*	n.a.	1.9E-08-1.3E-11	n.a.	524-534*		0.078-0.22*	sol (hot aromatics)
Methylanthracenes[1-]	1-MA	192.3		85	n.a.	n.a.	n.a.	1.05e	199-363			n.a.
Methylanthracenes[2-]	2-MA	192.3	202-208		n.a.	n.a.	n.a.	1.81 (0°C)	293-359#		0.019-0.042	n.a.
Methylanthracenes[9-]	9-MA	192.3	79-81.5		5.18-5.65	n.a.	n.a.	1.066		361*	0.26-0.27	n.a.
Methylchrysene[1-]	1-MCHR	242.3	247-257		6.48*	n.a.	n.a.	n.a.		461*		n.a.
Methylchrysene[6-]	6-MCHR	242.3	159-161.4	160.3	6.48*	n.a.	n.a.	n.a.		459*	0.065(ave.)	n.a.
Methylchrysene[5-]	5-MCHR	242.3	117.1-118	117.1	6.48*	n.a.	n.a.	n.a.		458*	0.062(ave.)	n.a.
Methylphenanthrene[1-]	1-MPHEN	192.2	118-123	123	5.17*	n.a.	1.3E-07-4.0E-04	n.a.	354.3-390		0.073-0.3	n.a.
3-nitrofluoranthene	3-NF	247.1	159-163	159-160	5.0*	n.a.	n.a.	n.a.			5.38*	n.a.
Nitropyrene[1-]	1-NP	247.3	150-157	155	4.77*	n.a.	n.a.	n.a.			8.6*	n.a.
Nitroacenaphthene[5-]	5-NACE	199.2	103-104		3.63*	n.a.	n.a.	n.a.			46*	n.a.
Perylene	PER	252.3	273-279		6.5	10.5	n.a.	1.35	497-503		0.0003-0.0008	n.a.
Phenanthrene	PHEN	178.2	100-101		4.38-4.84	3.7-4.0	1.6E-05-4.7E0-04	1.025		340	1.0-1.3	0.02##; 0.5b; 0.42$
Pyrene	P	202.3	149-156		5.03-5.32	1.1	9.1E-08-7.5E-08	1.28	360-404		0.13-0.16	n.a.
Quinoline	QUINOL	129.2		-19.2	2.03-2.08	n.a.	0.13 @ 59.7°C	1.096		237.7	60000	n.a.
Triphenylene	TRI	228.3	198.5-199	199	5.45	n.a.	5.0 (23°C)	n.a.	425-438		0.038-0.043	n.a.

Notes:

*	estimated
**	sublimes @ 435°C
#	sublimes @ 353°C
##	solubility in absolute alcohol
$	solubility in toluene
a	solubility (ppm) in acetic acid
b	solubility (ppm) in benzene
	Aqueous solubility @ 25°
	Solubility in other solvents @ 25°C
c	vap measurements @ 25°C
e	density measurements @ 99 C/4 torr

The following discussion on the chemical and physical properties is a summary of information from a recent publication on source emissions of polycyclic organic matter (U.S. EPA, 1987). More detailed treatments of transformation and fate in air and in condensed media appear in Chapters 6 and 8.

Polycyclic aromatic hydrocarbons are non-polar, high melting point, high boiling point compounds that are insoluble in water. In general, melting points range from a minimum near 100°C for phenanthrene to near 438°C for coronene. One exception to this general rule is benzo[c]phenanthrene, with a melting point of 68°C.

Factors that affect melting point include out-of-plane groups or fused rings. In general, PAH are planar compounds; however, in comparing perylene, benzo[a]pyrene, benzo[e]pyrene and benzo[k]fluoranthene, which are molecular isomers, perylene, the least volatile of the four (4) PAH with the highest melting point, also has the greatest number of vertical planes of symmetry.

The vapour pressures of PAH depend on the number of fused rings and molecular weight of the individual compounds. For example, phenanthrene has a vapour pressure of 9.1×10^{-2} Pa (3 rings and 14 carbons) and coronene a vapour pressure of 2.0×10^{-10} Pa (7 rings and 24 carbons). However, there are insufficient good vapour pressure data to quantify this relationship for all PAH.

The rate of adsorption of PAH on particulate matter is dependent on the vapour pressure of the PAH, the temperature, the surface properties and chemical composition of the particulate matter, as well as the absolute particle concentration in air. It is evident that these properties have a considerable influence on the adsorption characteristics and probably the subsequent reactivity of the PAH, as well as posing a problem during sample collection so that the analyte faithfully represents the sampled atmosphere.

With the exception of benzo[a]pyrene and some of the smaller molecular weight compounds, detailed chemical and physical property data for polycyclic aromatic hydrocarbons are scarce. Furthermore, there are several instances where the recorded values are several orders of magnitude different from each other for the same compound. For example, vapour pressure values for benzo[a]pyrene range from 6.7×10^{-6} to 7.3×10^{-7} Pa. Other examples show even greater deviations. As a result, it appears that the published data will only allow a qualitative assessment. For this reason, a sensitivity analysis of the data was proposed using the Mackay Level 1 fugacity model to help illustrate these observations and to assist in identifying those parameters that are of importance in evaluating environmental sources and fate data. Results from this sensitivity analysis are discussed in Chapter 8.

2.3 Chemical Reactivity

The chemical reactivity of PAH has been investigated theoretically and experimentally. The theoretical studies have focused primarily on the relationship between 'reactive' sites on the structure determined from molecular orbital calculations or empirical projections and various types of reactions. The experimental investigations have relied mainly on laboratory studies with simulated atmospheric conditions. From a comparative viewpoint, it is found that all PAH are more reactive than benzene and that their reactivity to methyl radicals increases with an increase in the number of alternating single and double bonds, that is, with greater conjugation (U.S. EPA, 1987). In general, increased conjugation leads to greater stability; however, it leads to greater reactivity toward free radical addition, e.g., methyl radicals. For example, compared to benzene, benz[a]anthracene, which has greater conjugation, reacts with methyl radicals 468 times faster (U.S. EPA, 1987). Similarly, electrophilic and nucleophilic reactions also occur more readily for PAH than for benzene, since ring attachment is accompanied by displacement of a proton to restore the stable aromatic system: this substitution mechanism is applicable to oxidation and reduction reactions on PAH and their facility can be explained empirically by the Le Chatelier Principle.

The atmospheric reactivity of PAH is influenced by temperature, light, oxygen, ozone, other chemical agents, catalysts and the surface area of the particulate matter on which the PAH are adsorbed. The reactivity of particle-bound PAH is limited by the lifetime of the particle in the atmosphere. Particles are removed from the atmosphere by sedimentation and wet scavenging processes. The effect of light on particle-bound PAH is also significant. For example, anthracene, phenanthrene, pyrene, benzo[a]pyrene and benz[a]anthracene show greater reactivities on alumina or silica gel than on fly ash from coal-fired furnaces. Furthermore, this reactivity is also influenced by the composition of the coal from which the ash is derived. Similarly, some early studies have shown that pyrene adsorbed on garden soil undergoes transformations that are temperature dependent as well as being influenced by U.V. radiation (Fatiadi, 1967). Indeed, such reactions contribute to the uncertainty that arises during ambient air or process sampling of PAH, since the species identified in the collected sample can correspond to a product formed by degradation of the sampled PAH (Brorstroem-Lunden et al., 1985), or by chemical transformation via atmospheric reactions with oxygen, ozone, NO_x and SO_x and nitric acid (Gibson, 1986).

The most recent reference that summarises the information on the reactivity of polycyclic aromatic hydrocarbons in the atmosphere was prepared for the United States Environmental Agency (U.S. EPA, 1987). An earlier, but equally useful review published by IEA Coal Research is also available (Smith, 1984). In the latter review, PAH reactivity is evaluated for atmospheric, land and water conditions. Some of the important conclusions were:

1. Anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, coronene, dibenz[a,c]anthracene, dibenz[a,h]anthracene and pyrene are readily oxidized on exposure to light when adsorbed on an aluminum oxide or silica gel matrix. On the other hand, chrysene, phenanthrene and triphenylene are unreactive under these conditions.

2. The products of photo-oxidation of adsorbed anthracene and pyrene are quinone derivatives, e.g., anthraquinone or 1,6[1,8]-pyrenedione.

3. No appreciable photodegradation occurs for anthracene, benzo[a]pyrene, fluoranthene, phenanthrene and pyrene on exposure to light when absorbed on coal fly ash. For example, the degradation for benzo[a]pyrene is only 15% when adsorbed on fly ash in contrast to 50% when adsorbed on alumina after the same exposure to light.

4. Adsorbed benzo[a]pyrene or anthracene on flyash appears to degrade in a similar manner with or without exposure to light;

whereas adsorption of pyrene on flyash led to stabilization towards photodegradation. There remained some uncertainty with regard to this effect on the degradation rate of exposure to light.

5. The chemical lifetime of PAH adsorbed on fine particles in the atmosphere is of the order of days, rather than hours.

In addition to the photo-oxidation processes discussed, the available information on chemical transformations was also reviewed (Smith, 1984). The information may be summarized as follows:

1. In general, most PAH containing a benzylic carbon atom (a saturated carbon atom attached to an aromatic ring), e.g., benzo[a]fluorene, benzo[b]fluorene, or fluorene, undergo spontaneous oxidation without light when adsorbed on coal flyash. For other compounds without a benzylic carbon atom, this simple evaluation is no longer applicable.

2. Polycyclic aromatic hydrocarbons will react with ozone as well as nitrogen oxides in the atmosphere to form oxy- and nitro-PAH, respectively. Less information is available on the reaction of PAH with sulphur oxides; however, there is evidence that PAH decomposition and ring splitting may occur during reactions with sulphur trioxide.

For PAH reactions in the soil and in water, the following review information was presented (Smith, 1984).

1. Polycyclic aromatic hydrocarbons will biodegrade by means of soil microorganisms to form PAH compounds that are less aromatic in

character. For example, benzo[a]pyrene is converted mainly to 9,10-dihydroxydihydrobenzo[a]pyrene as an intermediate by soil bacteria. Other PAH that are known to show similar characteristics are: benz[a]anthracene, benzo[ghi]perylene, benzo[e]pyrene, dibenz[a,h]anthracene, 7,12-dimethyl benz[a]anthracene, perylene and pyrene. The extent to which biodegradation occurred appeared to be independent of solubility.

2. PAH in solution or dispersed as sub-micron sols in water will selectively adsorb at the water/suspended matter interface; consequently, an increase in turbidity of waters containing PAH is associated with an increase in concentration of particle-bound PAH.

3. Volatilization does not play an important role in removing PAH from aquatic systems. Other processes such as adsorption, photolysis and biodegradation are more critical. Furthermore, since the particle-bound PAH gradually settle out and are deposited in sediments, such PAH are less susceptible to photochemical or biological oxidation.

4. Anthracene, benz[a]anthracene, benzo[a]pyrene and pyrene are rapidly transformed in water by the action of sunlight; however, chrysene, fluoranthene and phenanthrene photolyzed slowly.

2.4 Summary

The IUPAC nomenclature and structures for the forty-seven (47) priority polycyclic aromatic hydrocarbons are presented in this section. The chemical and physical properties are also summarized. The lack of reliable data and their variability are emphasized. Whereas some of the data for the physical properties have been peer-reviewed and are consequently accepted in such publications as IARC and the CRC Handbook of Physics and Chemistry, others are less reliable and are quoted in this report as the most commonly cited value or as a range of values. This range may correspond to several orders of magnitude in some cases. To reduce the uncertainty with regard to PAH fate and persistence in the environment which are directly dependent on these properties, a sensitivity analysis of the data is recommended using Mackay's level 1 fugacity model. This model is discussed in Chapter 8 of this report.

The chemical properties of PAH are also discussed with regard to their reactivity in the atmosphere, soil, water and sediments. It is believed the photo-oxidation and chemical transformations play a significant role for particulate and gaseous PAH in the atmosphere, whereas biodegradation and reactions controlled by particle size of the particle-bound PAH are more significant in soil, sediment and soil media.

3.0 SOURCES AND INPUTS OF PAH TO THE ATMOSPHERE

3.1 Introduction

Incomplete combustion of any organic material results in the production of a variety of chemicals, of which polycyclic aromatic hydrocarbons (PAH) are an example. These PAH are present in combustion emissions as either vapour-phase or particle-bound species and their relative abundances are largely, but not exclusively, governed by the temperature of the emission stream (Howard et al., 1984).

It is estimated that more than 90% of the particulate matter emitted from combustion sources is below 0.2 um in diameter and that the majority of PAH generated in these processes are adsorbed on particles 5.0 um or less in diameter (Handa et al., 1984). As a result, sampling techniques based on PAH capture on filters may not provide an accurate value of total PAH because the filter capture efficiency depends on particle size of the adsorbed PAH as well as the vapour/solid phase distribution.

3.2 Sources and Inputs

Polycyclic aromatic hydrocarbons are emitted to the atmosphere during the combustion or pyrolysis of organic materials. These sources can be separated into natural and man-made ones. The natural sources of PAH arise from forest fires, volcanic activity and possible biosynthesis by plants and microorganisms. Major man-made sources can be subdivided into point and non-point groupings. Point sources are not considered to be predominant contributors of PAH. These include processes such as power generation, coke production, petroleum catalytic cracking, aluminum production, incineration and carbon black production. Non-point sources include mobile sources, wood burning, oil burners as well as off road mobile sources such as tractors and farm equipment.

The total PAH emissions for the United States, Sweden and Norway are summarized in Table 3-1. They show that mobile sources are the major source in the United States corresponding to 35% of the total emissions. Industrial sources are responsible in the United States for 26% of the total PAH emissions (Bjorseth and Ramdahl, 1985).

PAH enter the aquatic environment through petroleum spills, runoff from roads and waste storage areas, atmospheric fallout, industrial effluents and by seepage from creosoted structures (Mix, 1984; NRCC, 1983; Neff, 1979). Neff (1979) estimated that the global aquatic PAH could be divided as follows: biosynthesis (1%); petroleum spillage (74%); domestic and industrial waste (2%); surface runoff (1%); and wet and dry atmospheric fallout (22%). Since petroleum tanker spills, offshore production leaks and natural seeps are more applicable to the world's oceans, the "petroleum spillage" component should be dramatically reduced with respect to Ontario.

The global estimates compiled by the National Research Council are presented in Table 3-2. The water-based component includes sources (e.g., tanker spills) that are not relevant to Ontario; however, the results indicate that atmospheric deposition may be the major source of PAH to Ontario waters.

TABLE 3-1

Estimated PAH Emissions

Source	PAH Emissions (MT/yr)			PAH Emissions (%)
	U.S.A.	Norway	Sweden	U.S.A.
Residential combustion	715	62.5	132	12.3
Industrial production	1,637	202.7	53.3	28
Power generation	401	1.3	0.5	7
Incineration (incl. forest fires)	1,150	13.7	3.5	19.8
Mobile sources	2,170	20	47	36
TOTAL	6,073	300	236	

From: Bjorseth and Ramdahl, 1985

TABLE 3-2

Global Estimated Inputs of Benzo[a]Pyrene and Total PAH to the Aquatic Environment from Various Sources

	Estimated Input (MT/yr)		
Source	Benzo[a]pyrene	Total PAH*	Percentage (Total PAH)
Atmospheric deposition	1,700	34,000	17 - 42.5
Water-based discharges	1-5	30,000-150,000	37.5 - 75
Land-based discharges			
Domestic and industrial effluents	17	1,400	0.7 - 1.8
Surface runoff	960	10,800	5.4 - 13.5
Spent lubricant disposal	1	190	0.1 - 0.2
Biosynthesis	24	2,700	1.3 - 3.4
Approximate total	2,700	80,000-200,000	

* Composition of "total PAH" was not present in original reference.

From: NRCC, 1983

After entry to the aquatic environment, there is rapid absorption of most PAH to particulate matter in the water column. While some PAH are taken up by biota, a large proportion is deposited to the sediments. More detailed discussion of these processes will be presented in Chapter 4.

3.3 Atmospheric/Terrestrial Sources and Input Data

Air emission factors for PAH are usually reported as a rate per unit of raw material consumed during production. These factors are then multiplied by average production or consumption rates to obtain the overall PAH emission rate to the environment.

Emission factors are generally based on a limited number of tests using a variety of sampling and analytical procedures. The lack of a standardized procedure makes it difficult to compare data from different research groups and accounts for the confusion in the reported data. The work on emission factors has been reviewed, NRC, 1983; U.S. EPA, 1987. The former report included a comprehensive compilation of emission factors from both mobile and stationary sources as well as other anthropogenic and natural sources; whereas the latter dealt with factors for polycyclic organic matter in general, including polycyclic aromatic hydrocarbons. PAH emissions from coal utilization have been extensively reviewed (Smith, 1984; Energy and Environment, 1987; and Bjorseth and Ramdahl, 1985). ORTECH International recently compiled a detailed set of emission factors for airborne toxics, including PAH, for Ontario MOE (ORTECH, 1988).

Polycyclic aromatic hydrocarbon emissions are characterized by specific PAH profiles for specific mixtures. Although it is recognized that source profiles will differ significantly from ambient levels because of atmospheric reactions, these profiles may be useful in evaluating their environmental impact and perhaps for the identification of sources based on ambient air measurements.

Other methods of source identification include:

- a comparison of binary PAH ratios; and
- the use of source markers, including substances other than PAH such as heavy metals, radiocarbon tracers, etc.

The method of using binary ratios requires the evaluation of characteristic PAH pair ratios to identify emission sources. Source markers, on the other hand, are tracers that are unique to, or almost exclusively emitted from, a particular source. They are not restricted to PAH species, as tracer elements such as lead and vanadium have been identified, and the total PAH concentration is then statistically correlated to these non-PAH. These concepts are referred to in the remaining chapters, where information is available.

3.3.1 Industrial Discharges

Petroleum refineries, steel mills, the wood preserving industry and coal processing operations have been documented sources of PAH in plant discharges in Ontario. Other industries that are possible contributors are the plastics and dyestuffs industries, gas works and lime processing (NRCC, 1983).

3.3.1.1 Coke Production

Coke is produced by the destructive distillation of bituminous coal and its major use is for steel production in Ontario. It is believed that in North America as a whole, 93 percent of the coke produced is used to convert iron ore to the metal (Radian, 1983). Iron foundries and chemical-producing plants account for the remainder (Smith, 1984).

By-product coke production is carried out in enclosed slot-type ovens. The major components of this process are:

- charging the ovens with pulverized coal;
- the coking reaction;
- mechanical 'pushing' of the coke into quench cars after coking is complete;
- water quenching of the hot coke; and
- by-product recovery.

At each stage of the process, fugitive emissions arising from leakages occur, often through badly-fitting coke oven doors (Smith, 1984). Battery stacks are located on the ovens to provide a natural draft of the combustion gas used to heat the battery and oven gases leak through the walls and are emitted via stacks. Emission factors for coke production are presented in Tables 3-3 and 3-4 based on data by Radian (1983); Smith (1984); ORF (1978; 1979); MOE (1980); Krugel (1979); Adamek (1980); Lao et al. (1979); Ortech, 1988; and MOE Air Emissions Inventory, 1985.

TABLE 3-3

Emission Factors for Coke Production

Process	Benzene-soluble Fraction mg/MT coal	B[a]P mg/MT coal
Charging	50,000 - 550,000	-
Door Leaks	4,200 - 260,000	2 - 1,400
Topside Leaks	4 - 50	-
Pushing	8,000 - 17,000	-
Quenching	11,000 - 2,800,000	0.5
Battery Stacks	1,600	2 - 20
Total	74,800 - 3,628,650	4.5 - 1,420

- no data

From Radian, 1983; U.S. EPA, 1987.

TABLE 3-4

Emission Profiles and Factors for Coke Production

Operation	PAH	Emission Factor (mg/MT coal)
Coke Quenching	Anthracene & phenanthrene	0.65
	Benz[a]anthracene & chrysene	0.3
	Benzo[c]phenanthrene	0.2
	Dimethylbenz[a]anthracene	0.3
	Fluoranthene	0.4
	Methyl anthracenes	0.4
	Methyl chrysenes	0.02
	Methyl fluoranthene & methyl pyrene	0.2
	Pyrene	0.3
	Total PAH	2.5 - 2.9
Door Leaks	Benzo[a]pyrene	1.0 - 1,400
	Total PAH	4,300 (control unknown)
	Total PAH	0.07 (ESP controlled)
Battery Stacks*	Benzo[k]fluoranthene	31
	Benzo[a]pyrene	55
	Benzo[ghi]perylene	25
	Fluoranthene	100
	Perylene	44

* Canadian emission factors

From: Ortech, 1988

TABLE 3-5

Summary of PAH Emission Factors for Battery Stack Emissions During Coke Pushing Operations in Ontario

Compound	Stelco[1] mg/MT coal	Dofasco[2] mg/MT coal	Algoma[3] mg/MT coal
Particulate	2,350	11,000	2,600
Fluoranthene	2.2	-	-
Perylene	1.6	3	-
Benzo[k]fluoranthene	1.2	-	-
Benzo[a]pyrene	1.4	-	-
Benzo[ghi]perylene	0.8	0.2	-
Total PAH	7.2	3	-

1. MOE, 1979; ORF, 1978
2. ORF, 1979b; MOE, 1980
3. ORF, 1979a

Notes:

[1] Emissions from Stelco controlled by wet electrostatic precipitator; Hamilton plant only.

[2] Emissions from Dofasco controlled by a venturi wet scrubber.

[3] Emission from Algoma controlled (control system not recorded).

- no data

Also reported in Table 3-5 are data compiled from stack tests on numbers 6 and 7 coke oven batteries at Stelco, Hilton Works (ORF, 1978; MOE, 1979); Dofasco, Hamilton Plant (MOE, 1980; ORF, 1979b); and Algoma, Sault Ste. Marie (ORF, 1979a). Results show that despite the high benzene soluble fraction, the PAH levels are low since the former includes a large contribution from naphthalenes.

The studies conducted at Stelco and Dofasco indicate that the most abundant PAH in coke oven emissions is fluoranthene.

A comparison of source profiles of coke oven emissions with mobile sources (gasoline) and residential coal heating indicates that benzo[a] pyrene/benzo[e]pyrene and anthanthrene/benzo[e]pyrene ratios are higher for coke oven emissions than for residential coal heating and that B[a]P is enriched in particulate matter for coke ovens in comparison to emissions from the other two sources (Daisey et al., 1986). These observations imply that in the Hamilton and Sault Ste. Marie regions for example, ambient B[a]P levels should be high compared to other regions in Ontario and that B[a]P/B[e]P and Anthn/B[e]P ratios are also relatively high. A summary table of particulate matter, PAH and B[a]P emissions from Stelco, Dofasco and Algoma is presented in Table 3-6.

According to the Ontario MOE Emission Inventory for 1985, the total particulate matter emission from coke oven operations in Ontario (four facilities) is about 1300 MT/y. If one assumes that the total PAH emission factor for Stelco (Hamilton) from Table 3-5 applies to the provincial emission inventory of total particulate emission from coking, the estimated emission quantities are:

PAH: 1300 MT/y x 0.0031 = 4 MT/y

B[a]P: 1300 MT/y x 0.0006 = 0.8 MT/y

TABLE 3-6

Estimated Values for PAH, B[a]P and Particulate Matter Emissions During Total Coking Operations in Ontario

	Particulate	PAH**	B[a]P***
Stelco (Hamilton)			
Yearly emissions (MT/yr)	281.2*	0.86	0.17
Stelco (Nanticoke)			
Yearly emissions (MT/yr)	139.8*	0.43	0.08
Dofasco (Hamilton)			
Yearly emissions (MT/yr)	681.6*	0.19	0.004
Algoma (Sault Ste. Marie)			
Yearly emissions (MT/yr)	189.8*	0.58	0.11
ESTIMATED TOTAL EMISSIONS (MT/yr)	1,292	2.1	0.4

* From: Ontario MOE Emission Inventory (1985). Presumed to be based on full nameplate production capacity.

** Calculated by assuming Particulate: PAH emissions ratios from Table 3-5. For Stelco 326:1; for Dofasco 3,667:1; and Algoma 326:1.

*** Calculated by assuming for Stelco, Dofasco and Algoma (Table 3-5) PAH/B[a]P levels = 5.1:1.

and so on, for the other measured PAH. Emissions of any PAH listed in Table 3-4 may be calculated similarly by using the emission factor relative to that of B[a]P.

Another way of estimating the PAH emission is based on estimated coal charging consumption and the emission factors shown in Tables 3-3 and 3-4. The following assumptions are used, derived from information in the references to Table 3-5.

Coal Consumption Data

Stelco (Hamilton) - Assume charge of 24.5 MT coal per oven and an average coking time of 17h. Assume 25 ovens (one-half capacity) are pushed during this period.

Stelco (Nanticoke) - Calculated from MOE particulate emission data and assuming an emission factor equal to that used for Stelco (Hamilton).

Dofasco (Hamilton) - Assume charge of 32.7 MT coal per oven and an average coking time of 16h. Assume 25 ovens (one-half capacity) are charged and pushed during this period.

Algoma (Sault Ste. Marie) - Assume charge of 16.1 MT coal per oven and an average coking time of 23h. Assume 25 ovens (one-half capacity) are charged and pushed during this period.

These assumptions lead to a calculated total quantity of coal consumption for coking in Ontario of about 1 x 10^6 MT/y at 50% capacity, a reasonable basis for emissions estimation.

The total PAH controlled emission factor resulting from the sum of emission factors shown in Table 3-4 is about 300 mg/MT coal.

These estimates lead to a total PAH emission of 0.3 MT/y, or 0.6 MT/y at full capacity.

Using the Bjorseth and Ramdahl (1985) total PAH emission factor of 15 g/MT coal yields an Ontario emissions estimate of 15 MT(PAH)/y. The level of control is not specified for this emission factor, but by comparison with Tables 3-3 to 3-5, it must refer to a largely uncontrolled emission. This is not the case in Ontario.

The coking emission estimates for total PAH by the various methods of calculation are then:

Source	Total PAH Emission
Ontario MOE Emission Inventory and Ontario source testing data	2.1 MT/y
Ontario MOE E.I. and Stelco only source test	4
Coal consumption estimate and Ortech emission factor	0.3-0.6
Coal consumption estimate and Bjorseth and Ramdahl (1985) E.F.	15

The most likely value is suggested to be in the range of the first two entries in the above table, i.e., 2 to 4 MT/y. B[a]P and other specific PAH emissions may be estimated from the data in Tables 3-3 to 3-6.

3.3.1.2 Metal Processing

The 'sintering' process, in which coke is burned to agglomerate the iron ore for feedstock to the blast furnaces, is also a source of PAH emissions to the atmosphere. Estimated B[a]P emission factors for this process range from 0.6 mg/MT sinter feed processed (U.S. EPA, 1987).

Iron foundries are recognized as another source of PAH emissions into the environment. Organic binders used in the molds consist of pitches, asphalts, oils and synthetic polymers. The organic binders decompose to form PAH during casting. PAH emission profiles factors for ferrous foundries and ferro alloy manufacture are presented in Table 3-7 (Ortech, 1988).

There are currently no aluminum smelters or anode plants located in Ontario. The closest installations are in Massena, New York, across the St. Lawrence River from Cornwall, Ontario, where both Reynold Metals Company and the Aluminum Company of America have smelting and casting operations. Any contributions to the overall Ontario PAH mass balance from the aluminum plants would occur by transboundary migration across the St. Lawrence River or short-intermediate range transport between the two borders.

3.3.1.3 Coal Liquefaction

There are no large-scale, continuous operating coal liquefaction plants in Ontario and no such plants are anticipated in the foreseeable future.

TABLE 3-7

Emission Factors for Foundries

Sector	PAH	Emission Factor (mg/MT)
Ferrous foundries (shakeout process)	Total PAH	7,700
Ferro alloy Manufacture*		
Si/Mn production	Anthracene & phenanthrene	2,000
	Benz[a]anthracene & chrysene	15
	Fluoranthene	230
	Fluorenes	1,400
	Methyl anthracenes	70
	Pyrene	210
	Total PAH	4,000

* Canadian emission factors

Data tabulated for scrubber controlled emissions.

From: Ortech, 1988.

3.3.1.4 Petroleum Refining (Catalytic Cracking)

Crude petroleum and many petroleum products contain an extremely complex mixture of several thousand organic compounds including many PAH (NRCC, 1983). The production of hydrocarbon fuels and other refined petroleum products results in the release of hydrocarbons in effluents, even after treatment.

Bitumen and fuel oils are derived from crude oils in the petroleum refining process. The heavy crude is distilled to produce various fractions of residuas and distillates. Selected fractions of the distillate are upgraded to distillate fuel by catalytic cracking (breaking up of long chain hydrocarbons); heavier fractions of the distillate crude are further processed to produce various grades of asphalt.

Catalytic cracking takes place in the presence of a catalyst that becomes deactivated through continual deposition of carbon, as coke, on active sites. The catalyst is then regenerated by combusting these coke deposits, which result in PAH emissions and thereby make catalyst regenerators a potential PAH source.

Three types of catalytic crackers are in use in the petroleum industry: fluid-bed, Thermofor and Houdriflow cracking units, and the latter two are based on a moving bed design. Most operations in Ontario are based on the fluid-bed design. Emission factors for fluid-bed units (FCC) are presented in Table 3-8, based on information reviewed in U.S. EPA, 1987.

TABLE 3-8

Mean Emission Factors for Fluid Bed Petroleum Cracking Catalyst Regenerators (controlled versus uncontrolled)

Compound	PAH Emission Factors Controlled (CO waste heat boiler) ug/barrel oil	 ug/GJ	 Uncontrolled ug/barrel oil	 ug/GJ
Benzo[a]pyrene	11	1.95	169	30
Pyrene	92	16.3	9,402	1,669
Benzo[e]pyrene	13	2.3	1,221	216.7
Perylene	ND	ND	ND	ND
Benzo[ghi]perylene	18	3.2	146	25.9
Anthanthrene	ND	ND	ND	ND
Coronene	ND	ND	ND	ND
Anthracene	ND	ND	690	122
Phenanthrene	ND	ND	133,333	23,663
Fluoranthene	59	10.5	6,735	1,195
Total	193	34.25	151,606	26,906

1 barrel = 0.159 m^3 oil

Assume average oil density = 0.83 - 0.92 MT/m^3 (Avg = 0.875 MT/m^3)
Calorific value: 40.5 MJ/kg = 40.5 GJ/MT

From: U.S. EPA, 1987

PAH profiles were reported in a study conducted for the U.S. Department of Energy by Warner, 1984. Table 3-9 summarizes PAH data for samples from an East Montreal refinery plume (PACE, 1984). Emission factors for petroleum refineries are presented in Table 3-10 (Ortech, 1988). Estimates for PAH loading for Ontario are presented in Table 3-10. The estimated annual PAH loading from Ontario refineries based on the 1986 data of crude oil transformed (26,685,100 kL) is 66.7 - 648 kg depending on the level of control.

3.3.1.5 Production of Pyrolysis Products (Coal Tar/Creosote/Anthracene Oil/Coal Tar Pitch/Carbon Black)

Crude coal tars are by-products produced in the carbonization process used to make coke and/or gas. The product of crude coal tar is closely related to the steel industry because it is a coke oven product.

A detailed study has been carried out at Domtar Chemicals coal tar distillation plant before upgrading the air pollution control system (Hamaliuk, 1987). Emission rates are presented in Table 3-11.

Carbon blacks are manufactured by the vapour phase pyrolysis of hydrocarbons. Production is usually based on the oil-furnace process to form carbon black and hydrogen: other feed materials used for carbon black production are natural gas and acetylene.

TABLE 3-9

PAH Concentration Range in the Plume
from the Three Refineries
Located in Montreal

PAH	Adsorbed PAH/ Particulate (mg/MT)
Anthracene/Phenanthrene	60
Methylanthracenes and Methylphenanthrenes	80
Benz[a]anthracene/Benzphenanthrenes	670
Methylbenz[a]anthracene	50-70
Acenaphthene	60-160
Fluorene	60
Benzothiophene	40-90

From: PACE, 1984.

TABLE 3-10

Average PAH Emission Factors and Total PAH Loading for Fluid Bed (FCC) Catalyst Regenerating Units for Petroleum Refineries

PAH	Emission Factors Uncontrolled (mg/kL)	Controlled (mg/kL)	Estimated Loading* (kg/yr)
Anthracene	5.8	N.D.	
Anthanthrene	N.D.	N.D.	
Benzo[a]pyrene	1.4	0.9	24-37
Benzo[e]pyrene	10.2	0.1	
Benzo[ghi]perylene	1.2	0.15	
Coronene	N.D.	N.D.	
Fluoranthene	56.5	0.5	
Perylene	N.D.	N.D.	
Phenanthrene	1,120	N.D.	
Pyrene	78.8	0.8	
Total PAH	24.3**	2.5***	66.7-648

* Based on 26,685,100 kL total crude oil transformed to refined products in 1986 (PACE Report 81-4, 1987). Estimates cover the range of "controlled" to "uncontrolled" emissions.

** Assume average oil density = 0.875 MT/kL; 28 mg/MT = 24.3 mg/kL.

*** Calculated from sum of average values for 10 PAH.

From: Ortech, 1988

TABLE 3-11

PAH Emission Rates from a Coal Tar Distillation Plant in Hamilton

Source	Emission Rate (kg/day)			Comments
	PAH(¹)	Benzene-sol Fraction	Total Particulate(²)	
Hotwell	0	3000	5780	1. Before upgrading scrubber system.
Wash Oil Tank (upset condition)	5	898	2090	2. Before incineration of emissions from the Wash Oil, Tar Mix and Pitch Tanks.
Tar Mix Tank	2	48	125	
Pitch Tanks	9	258	570	

(1) PAH include: acenaphthylene, acenaphthene, fluorene, anthracene, phenthrene, fluoranthene and pyrene.

(2) Sampled using the Montreal Urban Community cold trap method. Benzene soluble and total particulate fraction contain naphthalenes.

Personal Communication, Hamaliuk, G., Domtar Chemicals Ltd., 1987.

Emission factors for carbon black manufacturing in all cases are applicable to emissions from the main process vent (U.S. EPA, 1987). No data are available for raw product processes such as grinding, drying or packaging. Emission factors for polycyclic aromatic hydrocarbons produced during an oil-furnace carbon black operation are presented in Table 3-12. The major constituent are acenaphthene (42%), pyrene (26%) and methyl and dimethyl-substituted anthracenes/phenanthenes (12%) (Serth et al., 1980; U.S. EPA, 1987).

Bitumens are mainly used in hot-mix asphalt plants and roofing manufacturing. Hot mix asphalt, used primarily for road paving, is produced by mixing and blending of stone aggregates, sand and bitumen at 120°C to 180°C. Asphalt roofing products generally involve the impregnation of heavy paper felt with various types of asphalt. The major sources of PAH emissions from asphalt roofing manufacturing are the air blowing operation and the asphalt saturator. During air blowing, air is bubbled through hot asphalt at 220° to 290°C. Hot asphalt at 200-230°C is applied to the heavy felt by a spraying and/or dipping process at the asphalt saturator.

PAH emissions during asphalt production have been reported (Ortech, 1988). The major PAH identified were anthracene and phenanthrene, dibenzothiophene, methylanthracenes and methylphenanthrenes with emissions factors of 4.0, 3.6 and 6.9 mg/MT asphalt produced in Hot Mix plant operations. The total PAH emission factor was reported to be 19.7 mg/MT (Ortech, 1988). An earlier study reported particle-bound PAH emission rates of 1×10^{-4} g/hr for benzo[k]fluoranthene and 1.6×10^{-2} g/hr for chrysene (MOE, 1977).

TABLE 3-12

PAH Emission Factors from an Oil-Furnace Carbon Black Plant

Compound	Mean Emission Factor mg/MT
Acenaphthylene	800
Anthrancene/phenanthrene	70
Benzo[c]phenanthrene	<2
Benzofluoranthenes	30
Benzo[ghi]perylene	40
Benzopyrenes & perylene	30
Chrysene & benz[a]anthracene	9
Dibenzanthracenes	<2
Dibenzocarbazole	<2
Dibenzopyrenes	<2
Dibenzothiophene	14
Fluoranthene	60
Indeno[1,2,3-cd]pyrene	<2
Methylanthracene/phenanthrenes	100
Methylfluoranthene/pyrene	23
Pyrene	500
Total PAH (1)	1,900

(1) Includes other PAH not on the priority list.

From: U.S. EPA, 1987.

Gunkel and Bowles (1985) reported an emission factor of 1.07-0.25 ug/MT asphalt for 16 volatile organic compounds in a study of emissions from batch mix asphalt and drum mix asphalt plants. PAH that were detected included acenaphthylene, acenaphthene, phenanthrene, fluorene and pyrene.

3.3.2 Power Production Sources

3.3.2.1 Coal Mining (Coal Dust)

The presence of phenanthrene, pyrene, chrysene and perylene, as well as other PAH has been reported present in respirable coal dust (Setzer, 1979).

This result has been verified in work by other authors, in which thirteen (13) PAH were identified in the respirable dust fraction in coal mines (Shultz et al., 1972). As a source of PAH atmospheric emissions, coal mining plays an insignificant role, but amounts generated by fugitive emissions during loading from storage piles etc. are unknown.

3.3.2.2 Coal-Fired Power Plants

In 1979, it was estimated that coal accounted for 90% of the fossil fuel consumption for the generation of electric power in Ontario (MOE, 1979). Despite the predictions in the 1950s and 60s indicating that nuclear-powered stations would supersede this method, Ontario Hydro operates large coal-fired stations at Nanticoke, Lakeview and Lambton and smaller units at Atikokan and Thunder Bay to generate about 30% of total power production. At full load, Nanticoke is nominally rated for 4000 MW, Lakeview at 2400 and Lambton at 2000 MW. Atikokan and Thunder Bay are nominally rated at full load at 200 and 400 MW respectively. In general, these units are front- or tangential-fired with wet bottom furnaces or with a travelling grate spreader stoker.

A detailed examination of the data related to the method of firing and consequently rate of firing for units of different design was reported by Hangebrauck et al., 1967. The results indicated significant amounts of B[a]P, pyrene, B[e]P, benzo[ghi]perylene and fluorene regardless of the method of firing, as well as some variation in detectability of other PAH including, perylene, anthanthrene, coronene, anthracene and phenanthrene.

Another study also provided an emission factor database that distinguishes between vapour phase and particle-bound PAH (NRC, 1983). Data are reproduced in Table 3-13. Emission factors complied in a more recent study for the Ontario Ministry of the Environment are summarized in Table 3-14 (Ortech, 1988).

The emission profile, relative PAH emission rates for Ontario Hydro's Lambton and Nanticoke thermal generating stations are presented in Table 3-15 (ORF, 1986; Evans et al., 1985). Table 3-16 provides a summary of the estimated PAH and B[a]P emissions for Ontario Hydro's coal-fired generating stations.

TABLE 3-13

Average PAH Emission Factors for Differently-Fired Coal Power Plants

Unit	BSF		B[a]P	
	mg/MT	mg/GJ	ug/MT	ug/GJ
Vertically-fired dry bottom (1)	29.6	1140	0.003	0.12
Front wall-fired dry bottom (1)	8.3	320	0.0005	0.02
Tangentially-fired dry bottom (1)	16.1	620	0.003	0.13
Opposed, base-directed burners, wet bottom (1)	32.0	1230	0.003	0.13
Cyclone-fired wet bottom (2)	52	2000	0.009	0.35
Spreader stoker travelling grate (2)	27	1040	0.0005	0.02

BSF - benzene soluble fraction

(1) pulverized coal
(2) crushed coal

From NRC, 1983.

TABLE 3-14

PAH Emission Factors for Coal-Fired Thermal Generating Stations

PAH	Emission Factor* (mg/MT coal) Bituminous	Lignite
Acenaphthene	N.D. - 0.73	N.D.
Acenaphthylene	N.D. - 1.62	N.D.
Anthracene	0.11 - 2.22	0.3 - 0.54
Benz[a]anthracene	N.D. - 3.02	N.D. - 0.29
Benzo[b]fluoranthene	N.D. - 1.73	N.D. - 0.93
Benzo[k[fluoranthene	N.D. - 1.55	N.D. - 0.69
Benzo[a]pyrene	0.29 - 48	N.D. - 0.24 (2.0)**
Benzo[e]pyrene	0.13 - 0.28	0.69 - 0.95
Benzo[a]phenanthrene	N.D. - 0.51	0.39 - 4.0
Benzo[a]fluorene	0.73 - 3.9	0.1 - 0.3
Benzo[ghi]perylene	0.04 - 5.7	0.53 - 3.9
Chrysene	N.D. - 5.54	N.D. - 0.54
Dibenz[a,h]anthracene	N.D. - 5.0	N.D. - 0.36
Fluoranthene	N.D. - 15.65	0.05 - 0.66
Fluorene	N.D. - 2.68	0.15 - 0.18
Indeno[1,2,3-cd]pyrene	N.D. - 1.2	N.D. - 0.59
2-methylanthracene	0.15 - 2.5	0.6 - 0.93
9-methylanthracene	N.D. - 14	N.D.
9,10-dimethylanthracene	1.6 - 12	2.2 - 3.5
1-methylphenanthrene	0.54 - 7.1	0.3 - 0.44
1-nitropyrene	0.24 - 2.3	0.42 - 2.8
Phenanthrene	0.03 - 31.4	0.18 - 0.93
Pyrene	3.3 - 17.0	4.3 - 6.9
Triphenylene	N.D. - 0.11	N.D.
Total PAH	22 - 120 (28)**	26 - 31

* Canadian Emission Factors
** Average for an ESP controlled facility.

From: Ortech, 1988.

TABLE 3-15

Ontario Hydro Lambton and Nanticoke Thermal Generating Stations Emission Rates of Polycyclic Aromatic Hydrocarbons

Compound	Emission Rate (ug/s) Lambton[1]	Emission Rate (ug/s) Nanticoke[2,3]
Naphthalene	0.3	-
Acenaphthylene	0.3	-
Acenaphthene	0.68	-
Fluorene	2.0	-
Phenanthrene	28.9	6.7
Anthracene	0.92	27
Fluoranthene	21.4	-
Pyrene	9.8	443
Benzo[a]anthracene	6.3	-
Chrysene	10.5	-
Benzo[b]fluoranthene	5.5	-
Benzo[k]fluoranthene	5.5	-
Benzo[a]pyrene	3.4	115
Benzo[e]pyrene	-	11.4
Indeno[123-cd]pyrene	0.66	13
Dibenzo[ah]anthracene	0.24	137
Benzo[ghi]perylene	0.78	49.3
Total	97.2	1835

1 ORF (1986)
2 Evans et al. (1985)
3 Mean of two runs.

TABLE 3-16

Estimated PAH, B[a]P and Total Suspended Particulate (TSP) Emissions for Ontario Hydro's Coal-Fired Power Generating Stations

Utility	Coal Type	Coal Consumption (MT/yr)*	PAH** (MT/yr)	B[a]P (MT/yr)	TP*** (MT/yr)
Nanticoke	Bituminous	5,807,000	0.16	0.01	4,200
Lakeview	Bituminous	1,353,000	0.04	0.002	1,100
Lambton	Bituminous	2,962,000	0.08	0.006	3,200
Thunder Bay	Bituminous	1,228,000	0.03	0.002	260
Atikokan	Lignite	612,000	0.02	0.0001	140
Total Emissions			0.33	0.21	8,400

* 1987 figures

** Data from Ortech, 1988 (Table 3-14 of this report).

*** Total particulate matter from Ontario Hydro report to MOE, Jan. - Dec., 1987. This figure includes contributions from oil consumption in power generation for 4 of the 5 stations.

Assumed B[a]P emission factor for bituminous coal = lignite coal factor = 2 mg/MT.

3.3.3 Municipal and Hazardous Waste Incinerators

Only limited data are available on the release of polycyclic aromatic hydrocarbons from facilities of this type. Ontario based data are virtually non-existent; results from SWARU were reported to be very low in the Ontario PAH source survey (MOE, 1977); so low as to make the data suspect (0.5-1.5 ng/m^3 of benzo[k]fluoranthene and benzo[a]pyrene). More recent data are available from the National Incinerator Testing and Evaluation Program (NITEP) and other municipal solid waste (MSW) incinerator sampling programs. These data are presented in this section. SWARU and the London Victoria Hospital EFW incinerator are the only two operating municipal incinerators in Ontario at present.

Few data on hazardous waste incinerator emissions are available; however, values obtained for the Tricil incinerator in Sarnia have been reported and are summarized in Table 3-17 (ORF, 1987). The Ontario Research Foundation report on the Tricil unit suggests that the stack flow is approximately 17.5 m^3/s with 27% moisture at 216°C and 13.8% O_2.

Apartment incinerators are currently prohibited in the province. They have been largely uncontrolled and poorly maintained in the past. No data are available for PAH from this source.

Biomedical incinerators in most facilities are similar to the batch-fed, multi-chamber incinerators used in apartments. The units are likely better maintained than apartment units, but the majority of the units do not meet MOE combustion guidelines (CSC, 1987).

TABLE 3-17

PAH Emission Data for TRICIL Hazardous Waste Incinerator (ng/Rm^3 @ 11% O_2)

Compound	PAH Concentration (ng/Rm^3)
Acenaphthylene	160 - 310
Acenaphthene	170 - 460
Anthracene	250 - 870
Benz[a]Anthracene	80 - 420
Benzo[b]Anthracene	7 - 20
Benzo[b]Fluoranthene + Benzo[k]Fluoranthene	70 - 320
Benzo[a]Fluorene	20 - 120
Benzo[b]Fluorene	7 - 120
Benzo[ghi]Perylene	110 - 260
Benzo[a]Pyrene	40 - 110
Benzo[e]Pyrene	1.5 - 10
Chrysene + Triphenylene	170 - 740
Coronene	30 - 190
Dibenz[ac]Anthracene + Dibenz[dh]Anthracene + Picene	10 - 70
Dibenzo[ac]Pyrene	6 - 40
9,10-Dimethylanthracene	N.D.
7,12-Dimethylbenz[a] anthracene	100 - 500
Fluoranthene	950 - 3900
Fluorene	320 - 990
Indeno[123-cd]Pyrene	70 - 230
2-Methylanthracene	
1-Methylphenanthrene	410 - 1200
9-Methylphenanthrene	80
Perylene	10 - 40
Phenanthrene	2500 - 7300
Quinoline	
Total	6460 -- 21010

N.D. no data
From: ORF, 1987.

Some hospitals have semi-continuous units of the starved air modular type. Some data from a unit of this type in British Columbia indicates total PAH levels in the range of 6.1 ug/Rm^3 @ 11% O_2.

Three NITEP studies have been completed at Charlottetown and Quebec City, as well as an air pollution control (APC) test in Quebec City. PAH data from these systems under normal operating conditions are summarized in Tables 3-18 and 3-19 (NITEP, 1985; 1988).

It is generally thought that PAH levels will be a function of particulate matter levels; however, Table 3-18 shows no consistent relationship between these parameters.

Total PAH data from Quebec City (Table 3-19) illustrate the influence of low temperatures as well as the fact that poor air distribution does not produce a significant change in total PAH levels.

The total PAH values for PEI incinerator ash are 1.2-4.7 ug/g; for the boiler the value is 0.03 ug/g and for the economizer 0.01-0.07 ug/g. It is estimated that incinerator ash may total 15% of the feed excluding glass and metal; boiler and economizer ash 0.07% of feed.

Quebec City values were 0.1-0.5 ug/g incinerator, 0.02-0.07 ug/g boiler and 0.1-0.3 ug/g for the precipitator. Typical APC levels were 0.3-2.0 ug/g maximum of total PAH. The incinerator ash at Quebec City is approximately 25% of the total feed including glass and metal, boiler 0.5% and precipitator 0.8%.

TABLE 3-18

NITEP PAH Emission Data and Levels in Incinerator Ash

	PAH Emissions (ng/Rm^3)	Ash Concentrations (ng/g)		
		Incin.	Bottom	Exit
Acenaphthylene	70	37	-	5
Acenaphthene	80	28	-	-
Fluorene	360	150	4	1
Phenanthrene	1630	541	21	21
Anthracene	590	53	1	4
Fluoranthene	390	113	3	15
Pyrene	310	146	3	8
Chrysene	10	37	-	1
Benzanthracene	130	39	5	9
Benzene, pyrene & fluorene	170	51	-	-
Indenopyrene	20	3	-	4
Dibenzanthracene	7	4	-	4
Benzperylene	3	5	-	3
Total PAH	3750	1206	38	73
Total Particulate Matter (mg/Rm^3 @ 11% O_2)	150			

From: Vol. I NITEP Charlottetown Testing Program, 1985.

TABLE 3-19

Group Test Averages for Stack Sampling Results

Quebec City NITEP Combustion Tests

Test Condition	Total Particulate Matter (mg/Rm^3 @ 11% O_2)	Total PAH (ug/Rm^3 @ 11% O_2)	Ash Data Total PAH (ng/g) Incinerator Wet Rate (% of refuse)	Boiler Rate (% of refuse)	Precipitator Rate (% of refuse)
Good Conditions (Feed Rate MT/hr)					
Design Burning Rate (8.9)	16	2.9	538 (27.2)	25 (0.4)	111 (0.6)
Poor Conditions Design Burning Rate					
Low Temperature (9.6)	40	15.8	155 (26.4)	33 (0.4)	122 (1.4)
Poor Air Distribution (8.7)	45	2.3	320 (23.8)	69 (0.6)	331 (1.4)

From: Volume II NITEP Quebec City Combustion Tests by Lavalin Inc., 1988 (in press).

A comparison of the PAH emission factors and emission profiles for MSW, industrial liquid waste and commercial incinerators treating hazardous waste is presented in Table 3-20.

Currently in use or contemplated(*) are the following facilities: London Victoria Hospital, 273 tpd starved air with APC; Peel*, 364 tpd starved air with APC; Toronto Refuse-fired Steam Plant*, 1700 tpd mass burn with APC; SWARU 480 tpd with APC; and Trintek* 500 tpd starved air with APC. The Commissioners Street, 273 tpd unit has been mothballed and will probably not be recommissioned.

Other projects are being investigated in Ottawa, Guelph, Windsor and Kingston. These units will probably have a design similar to Peel, except for Ottawa which will have a mass burn system.

Based on the currently operating and planned incinerator facilities, the estimated PAH loading to the atmosphere is 1.4 MT/yr; data for each incinerator are compiled in Table 3-21.

3.3.4 Transportation

Gas-phase and particulate polycyclic aromatic hydrocarbons are major components in the emissions from internal combustion engines. Some nitro-substituted PAH are believed to form in the exhaust through reaction of the PAH and nitrogen oxides. The emission rates and PAH profiles are dependent on the temperature of the combustion chamber and exhaust system and consequently on engine size, design, working load and operating speed (U.S. EPA, 1987).

TABLE 3-20

Summary Table of PAH Emission Factors from MSW Industrial Liquid Waste and Commercial Incinerators

PAH	Emission Factors (mg/MT feed) MSW Incinerators	Industrial Liquid Waste Incinerators	Commercial Incinerators
Acenaphthene	12	3.6	-
Acenaphthylene	1,000	2.7	-
Anthracene	-	5.8	104-190
Anthanthrene	-	-	14.6-174
Benz[a]anthracene & Chrysene	3.1	3.0	-
Benzo[a]pyrene	24	1.0	117-573
Benzo[e]pyrene	-	1.5	99.2-573
Benzo[b,j&k]fluoranthene	78	2.5	-
Benzo[ghi]perylene	14	2.1	198-1,918
Chrysene & triphenylene	62	5.5	-
Coronene	0.2	1.3	46.3-463
Dibenz[a,h]anthracene & dibenz[a,c]anthracene	0.11	0.6	-
Fluoranthene	140	24.8	458-8,600
Fluorene	68	6.7	-
Indeno[1,2,3-cd]pyrene	0.77	1.9	-
Phenanthrene	426	50.2	130-309
Perylene	0.77	0.3	6.8-132
Pyrene	168	14	706-9,261
2-methylanthracene	-	18.9	-
1-methylphenanthrene	-	8.5	-
9-methylphenanthrene	-	0.3	-
Total PAH	1,160*	374	1,910-22,200

- no data

* Column does not add to total because of differing databases for average values for individual PAH.

From: Ortech, 1988.

TABLE 3-21

Estimated Annual PAH Atmospheric Emissions to the Ontario Environment from Incinerators

Facility	Feed (MT/yr)	PAH Emission Factor (mg/MT feed)	PAH Emission Loading (MT/yr)
London Victoria	91,250	1,160	0.10
Peel*	120,450	1,160	0.14
Toronto Steam Plant*	562,100	1,160	0.65
Trintek*	164,250	1,910	0.3
SWARU	159,140	1,160	0.18
Total PAH			
Existing			0.3
Proposed			1.1

* Proposed installations.

The PAH emissions are diluted approximately 1000-fold after being exhausted and are cooled very rapidly. For example, the combustion of an efficiently-operated gasoline engine operates around 3500°C with exhaust temperatures between 400° and 600°C, whereas, for diesel engines, the corresponding tempeatures are 2000°C and 200 to 400°C respectively. It is estimated that within a few seconds, exhaust emissions are rapidly dispersed and cooled to ambient tempertures (U.S. EPA, 1987).

Heavier PAH, e.g., B[a]P, are present in mobile source emissions mainly as sub-micron particle-boud species, with the lighter PAH in the vapour phase. Engine oil accumulates PAH, which then leaks into the combustion chamber or exhaust system, thereby enhancing these levels in the emissions. It is estimated for the United States that 28 to 36 percent of B[a]P, B[a]A, CHR and P in engine oil that leaks into an automobile combustion chamber or exhaust system is emitted to the atmosphere (Handa et al., 1979).

Internal combustion engines without oil crankcases include two-stroke engines used for motorcycles, outboard motors, lawnmowers and chainsaws that are operated on a mixture of oil and gas. Because of their mode of operation, it is probable that PAH levels in the oil are in direct relation to PAH levels in the emissions. Typical PAH identified in such emissions are: fluorene, anthracene, pyrene, benz[a]anthracene, benzo[a]pyrene and benzo[ghi]perylene. It is estimated for the United States that the contribution from motorcycle emissions to the total PAH emissions from mobile sources in 1979 were less than 0.3 percent (NRC, 1983). There is a general trend toward fewer motorcycles in the United States and in Canada, in favour of passenger automobiles; therefore, the PAH contribution from motorcycles and two-stroke engines in general is probably insignificant compared to other sources and emissions from two-stroke engines are therefore only briefly discussed in this report.

There are few data on aircraft turbine engines, specifically particulate emissions from the combustion of kerosene fuels in gas turbines. PAH detected in studies of these emissions were: fluorene, anthracene/ phenanthrene, methylfluorene, fluoranthene, pyrene, acenaphthylene, benzofluoranthene, chrysene, benzopyrenes (mainly as benzo[e]pyrene) and perylene (Robertson et al., 1980). An emission factor of 30 ug B[a]P/kg fuel consumed has been reported by Smith, 1984.

3.3.4.1 Gasoline- and Diesel-Powered Vehicles

Because of the operating temperature and difference in engine design, diesel engines emit from 30 to 100 times more particulate matter by mass than gasoline engines, over 90 percent of which is below 0.1 um in aerodynamic diameter (NRC, 1983).

A list of compounds present in particulate matter exhausted from gasoline and diesel powered sources is given in Table 3-22. It is concluded that a higher level of nitro-substituted PAH is present in diesel-powered sources than in gasoline-powered sources. This is related to PAH reactivity in the exhaust with nitrogen oxides at the exhaust temperatures (U.S. EPA, 1987).

A detailed list of emission factors for light gasoline- and diesel-powered engines is presented in Table 3-23. Estimates for total PAH produced from this source are presented in Table 3-24.

TABLE 3-22

Polycyclic Aromatic Hydrocarbons Detected on Gasoline and Diesel Exhaust Particles

Gasoline Powered (1)	Diesel Powered (2)
	Acenaphthene
	Fluorene
Phenanthrene	Phenanthrene
Anthracene	Anthracene
Methylphenanthrenes/ anthracenes	Methylphenanthrenes
Fluoranthene	Fluoranthene
Pyrene	Pyrene
Methylpyrene	Methylpyrenes/fluoranthenes
Benzo[a&b]fluorene	Benzo[a&b]fluorene
Benz[a]anthracene	Benz[a]anthracene
Chrysene & Triphenylene	Chrysene & Triphenylene
Benzo[b,j&k]fluoranthenes	Benzo[b,j&k]fluoranthenes
Benzo[a]pyrene	Benzo[a]pyrene
Benzo[e]pyrene	Benzo[e]pyrene
Perylene	Perylene
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene	Benzo[ghi]perylene
Anthanthrene	Anthanthrene
Coronene	Coronene
	Methylfluorenes
	Dibenzothiophene
	Dibenzo[a,h]anthracene
	Nitropyrenes/fluoranthenes
	Nitrofluorenes
	Dinitrofluorenes (tent.)

(1) Alsberg et al., 1985
(2) Li-Yu et al., 1981; Tong et al., 1984; and Schuetzle et al., 1981.

TABLE 3-23

Emission Factors for Gasoline and Diesel Powered Mobile Sources

Emission Factors (mg/kL)

PAH	Gasoline Leaded**	Unleaded*	Unleaded#	Heavy-Duty	Diesel Light-Duty	Heavy-Duty	Motorcycle
Anthracene	200	54	13	591	696	-	592
Phenanthrene	4.9	220	52	2,400	2,600	-	2,400
Methylphenanthrene	1,500	275	32	1,500	1,760	-	294
Fluoranthene	360	115	27	1,257	1,860	200	1,257
Pyrene	718	30	34	1,593	2,335	-	1,593
Benzofluorene	-	36	4	200	233	-	61
Benzanthracene	97	29	1	61	217	83	86
Triphenylene	-	9.3	1	50	59	-	50
Cyclopentapyrene	35	120	14	653	768	-	653
Chrysene	204	23.5	5	248	391	-	248
Indenopyrene	12	9.3	0.1	0.06	149	79	0.06
Methylchrysene	185	32.5	4	177	-	-	-
1-nitropyrene	0.9	0.7	0.3	1	72	6.7	0.9
Benzofluoranthene	185	32.5	4	177	313	93	198
Bezo[e]pyrene	41	9.0	2	86	101	-	86
Benzo[a]pyrene	31	9.9	2	72	101	62	72
Perylene	5.8	1.6	0.3	7	8	-	7
Anthanthrene	-	-	-	-	-	-	-
Dibenzanthracene	21	3.7	0.5	21	25	9.4	21
Coronene	41	22	3	133	142	-	133
Benzoperylene	-	-	-	-	235	130	191
9-nitroanthracene	-	-	-	-	-	5	-
7-nitrobenzanthracene	-	-	-	-	-	1.2	-
6-nitrochrysene	-	-	-	-	-	<0.2	-
Total PAH		1,970	233	9,290	11,960	-	7,990
TSP***	193,478		101,346		1,726,790		

Data from Ortech International, 1988. Collated from six (6) primary and review references.

** no catalyst
* with oxidation catalyst
# with 3-way catalyst
*** Data from U.S. EPA, 1987. Estimated by assuming an average gas consumption rate of 7 km/L.
- no data

TABLE 3-24

Estimaies of Yearly PAH Emissions from Transporation Sources in Ontario

Fuel Type	Number (fleet)*	Gas Consumption (kL/yr)**	PAH Emission Factor (mg/kL)	Total PAH (MT/yr)
Gasoline				
Automobiles & Light Trucks				
- leaded	444,492	5,609,100	4,578	25.7
- unleaded (oxid)	3,303,188	8,504,647	1,970	16.8
(3-way)	610,088	1,570,780	233	0.37
(heavy-duty)	881,342	2,269,172	9,290	21.1
2-stroke engines (motorcycle, snowmobile, moped)	407,085	ND	7,990	-
Diesel				
Automobiles	33,872	1,932,000+	11,960	20.5
Heavy-duty/Commercial	127,652		9,240	
Jet Fuel				
Airline jets	306,608/yr++	-	2-10 B[a]P (mg/min)	0.028 as B[a]P

ND no data available for 2-stroke engine gas comsumption. The total gasoline consumption includes this volume and are included in the values considered under autombiles and light trucks.

* MOT, 1987. Registrant/Plate/Vehicle Population Statistics. Environment Canada, 1989. Private communication Lavallee, F. Percentage distribution of automobiles with 3-way, oxidation catalysts and no catalytic converters in Canada.

** Statistics Caanda, 1987. Catalogue 57-004.

+ MOE, 1989. Private communication, Rohac, I. 1986 estimate for diesel, oil consumption in Ontario.

+ + Aviation Statistics Centre, 1987. Aircraft movement statistics. 1987 annual report. Number of take-offs and landings per year.

3.3.4.2 Tire Wear

Particle-bound and vapour phase PAH are continuously released from tires during the normal operation of a vehicle. An emission factor of 0.14 g/d per million people was similarly estimated for B[a]P (U.S. EPA, 1987).

3.3.4.3 Source Markers (Transportation)

PAH profiles from car exhaust streams were reviewed by Daisey et al., 1986 and an attempt was made to identify characteristic PAH ratio pairs and fingerprint compounds. The profiles indicated high levels of phenanthrene, pyrene, chrysene and anthracene. Cyclopenta[1,2,3-cd]pyrene was identified as a potential source marker for vehicle exhaust since it was present in vehicle exhaust in larger amounts (Daisey et al., 1986) compared to other sources, such as coke oven and oil burning. Benzo[c]phenanthrene, benzo[ghi]perylene and coronene were also observed to be enriched in samples collected in a tunnel (Daisey et al., 1986).

Hering et al. (1984), have also identified the following as signature PAH compounds and heavy metals for sub-1.3 um sized particulate matter collected from a 1983 California vehicle fleet consisting of 3-6% diesels. These were: dibenzanthracene, benzo[ghi]perylene, indenopyrene, benzo[b&k]fluoranthene, lead, zinc and iron. Results indicated an increased level of benzofluoranthenes for an increase in the number of diesels, whereas benzo[ghi]erylene, indeno[1,2,3-cd]pyrene and dibenzanthracene were independent of the diesel population.

A study conducted by Harrison and Johnston (1985), on the deposition of PAH with lead, cadmium and copper particulate in the U.K. indicated that allowing for temporal variations, the fluxes for these compounds and elements, particularly lead, were elevated close to a major hghway and decreased to background levels within 20-40 m; however, with the reducing use of lead as anti-knock additives in gasoline, this conclusion is no longer applicable.

From these results, it can be inferred that when emissions from mobile sources are compared with emissions from other sources then higher levels of heavy metals such as lead, zinc, iron, cadmium and copper are present for mobile sources. In addition, the level of benzo[b&k]luoranthenes increases with an increase in diesel to gasoline vehicle traffic volume in areas of low solar intensity which tends to reduce PAH chemical reactivity. Also, the level of nitro-substituted PAH, particularly nitro- and dinitro-pyrenes increases with an increase in diesel to gasoline vehicle traffic volume.

3.3.5 Residential Heating

Extensive studies on the emissions from woodburning fireplaces as well as wood and oil-burning stoves and furnaces have been conducted (Hall and De Angelis, 1980; Ragland et al., 1985). Detailed reviews have also been presented (NRC, 1983; Smith, 1984; Nero & Assoc., 1984) including a review for Health and Welfare Canada by Concord Scientific (Davis, 1987).

3.3.5.1 Emission Factors

It is estimated that the emission factor for polycyclic organic matter, of which PAH form a component, is 5×10^{-4} to 0.2 g/kg, and the associated B[a]P emission factor is 4×10^{-5} - 0.0025 g/kg for woodburning fireplaces and stoves in the United States (Lipfert and Lee, 1985). The emissions are affected by appliance type, condition and type of wood fired, the rate of burn and measurement method, which is one of the reasons for the large range in values.

Particulate emission factors for unvented kerosene heaters were estimated by Ragland et al. (1985), and ranged from 11.8 to 25.3 mg/kg fuel for particulate and 0.6 to 54 ug/kg for total PAH emissions. Studies were conducted on both radiant and convective heaters.

Average values for emission factors for different fuels, appliances and operating conditions have been reported (Smith, 1984). These values are reproduced in Table 3-25. An emission source profile from both wood and treated lumber in woodburning stoves is presented in Table 3-26.

For both northern and southern Ontario, approximately 37% of households burned wood. This translates to an average yearly consumption of 5.1 full chords per household (10.2 MT) in northern Ontario and 3.7 full chords (7.4 MT) in southern Ontario (MacLaren, 1985).

Based on an emission factor of 29-40 mg PAH/kg and 0.5-0.7 mg B[a]P/kg wood consumed for residential heating and an estimated 35,700 households in northern Ontario and 255,000 households in southern Ontario burning wood, the estimated annual PAH emissions for Ontario from this source are 65-90 MT and the B[a]P emissions are 1.1-1.6 MT.

TABLE 3-25

Typical Emission Factors for Residential Heating

Fuel	Type	Total PAH (mg/kg)	B[a]P (mg/kg)
Oil (30 kW)	Stove	0.15	0.0022
Oil (7.5 kW)	Stove	10	-
Gas (210,000 Btu/hr)	Furnace	13 (ug/m^3)	1 (ug/m^3)
Gas	Furnace	65 (ug/m^3)	-
Oil	Furnace	0.15	0.0022
Oil	Furnace	0.13	-
Wood	Stove	40	0.5
Wood	Fireplace	29	0.7

From: Smith, 1984; Radian, 1983; Hangebrauck et al., 1967.

TABLE 3-26

Emission Profiles and Factors for PAH from Different Fuels in a Conventional Wood Stove

Compound	Emission Factors (mg/GJ) Wood	Emission Factors (mg/GJ) Treated Lumber
Anthracene	395	1100
Benz[a]anthracene	3.9	185
Benzofluoranthene	<1	<1
Benzo[ghi]perylene	2.7	16.3
Benzo[a]pyrene	39.5	131
Benzo[e]pyrene	32.9	147
Chrysene	105	81.7
Coronene	<1	32.7
Dibenz[a,h]anthracene	<1	NA
Fluoranthene	244	687
Fluorene	308	103
Methylanthracene	144	27.2
Methylphenanthrene	967	583
Perylene	52.5	16.3
Phenanthrene	644	1820
Pyrene	171	545

From: KHM, 1983; Smith, 1984.

3.3.5.2 Emissions (Oil and Gas Heating)

Oil and gas furnaces are commonly used in Ontario households to heat water and recirculating air. Gas furnaces burn a premixed mixture of gas and air and generally emit relatively small amounts of PAH per unit of heat input.

On the other hand, oil fired units introduce the fuel by pressure atomization or vaporization and, in comparison, relatively larger PAH emission rates per unit of heat input are produced. That is oil heating produces about 4 mg (POM)/GJ compared with 1 mg (POM)/GJ for gas (Peters, 1981).

PAH emission factors have been estimated for various types of oil and gas fired furnaces (NRC, 1983; Radian, 1983). These values are also listed in Table 3-25.

The 1979 MOE report identified commercial and institutional boilers (primarily oil- and gas-fired) as the main contributors to PAH emissions in the category of heat and power generation. Residential furnaces (oil- and gas-fired) were estimated to contribute little to the provincial total PAH emissions. Recent emission factor compilations (e.g., Table 3-25 and Ortech, 1988) indicate no significant changes in emission factor estimates relative to the data used for MOE (1979). Assuming no increase (or decline) since 1976, the base year of that study, in the use of coal for industrial boiler use, about 25% increase in the use of residual and distillate oils for residential, industrial, commercial and institutional heating and a 50% increase in gas utilization for these purposes, the total PAH emission from heat and power generation from residential heating, industrial, commercial and institutional boilers is estimated to be no more than about 2 MT/y. These sources are distributed throughout Ontario. In the context of the current assessment, these sources, then, would appear to be insignificant. They are not addressed in detail in this report.

3.3.6 Open Burning of Biomass

The emissions from open burning of biomass, which includes sources such as uncontrolled forest fires, prescribed refuse and agricultural waste burning, may contribute significantly to the PAH content of the atmosphere. However, there are few recorded data on emission factors for these sources.

3.3.6.1 Burning of Treated Wood Waste

Emissions from the burning of railway ties were studied during a test burn (Becker et al., 1984). The burn was conducted under controlled meteorological conditions with approximately 681 kg of creosote treated wood doused with #2 fuel oil and ignited with a railroad flare to simulate the practice of Burlington Northern Railroad. While the practice used by Canadian National and Canadian Pacific in Ontario is unknown, no other data for the burning of railway ties were available.

PAH detected during the test burn are presented in Table 3-27 as fractions of the total suspended particulate concentration. An average total suspended particulate emission rate of 3.68 kg/h was estimated for these burns, resulting in an emission factor of 10.6 g/kg of wood burned, assuming that all the PAH were generated during the first two hours of the burn.

TABLE 3-27

Derived Emission Factors for the Burning of Creosote Treated Railway Ties

Compound	[PAH/TSP] x 1000	Emission Factor (g/MT ties)
Total suspended particulate	-	10,600
Acenaphthylene	0.62	5.7
Acenaphthene	2.88	27.1
Phenanthrene	0.09	0.9
Anthracene	0.02	0.2
Fluorene	0.29	2.8
Pyrene	0.36	3.3
Chrysene	0.18	1.7
Benz[a]anthracene	0.88	8.3
Benzo[b]fluoranthene	0.54	5.1
Benzo[k]fluoranthene	0.16	1.5
Benzo[a]pyrene	0.59	5.5
Dibenz[a,h]anthracene	0.45	4.2
Benzo[ghi]perylene	0.09	0.9

Discussions with Canadian National environmental staff suggest that majority of the non-usable railroad ties are now disposed in secured landfill sites and only a small percentage is burned. Furthermore, the use of burning as a means of disposal is to be phased out in the early 1990's.

3.3.6.2 Forest Fires

Only limited data on PAH emissions from prescribed or uncontrolled forest fires are available. The most frequently cited work was based on simulating forest burning conditions in the laboratory by burning various loadings of pine needles on a metal table equipped to change slope and to take into account wind effects. The airborne, suspended particulate matter generated in this manner was collected on a glass fibre filter using a modified high-volume sampler and analyzed by gas chromatography/ mass spectroscopy (McMahon and Tsoukalàs, 1978).

PAH emissions from forest fires are dependent on the type of vegetation burned; the burn conditions; e.g., back fires, in which the fire perimeter spreads against the wind; or head fires, in which the fire perimeter moves with the wind; fire intensity and combustion phase (smoldering or flaming); as well as weather conditions. In general, the majority of uncontrolled (wild) fires in Ontario are head fires with a small backing component; however, this ratio is not known (Ward, Ministry of Natural Resources, 1989).

Emission factors for the polycyclic aromatic hydrocarbons detected in the simulated burn of pine needles are presented in Table 3-28.

TABLE 3-28

Emission Factors of Polycyclic Aromatic Compounds for Burning Pine Needles
(mg/MT fuel, dry weight)

	Fire Type & Fuel Loading					
	Backing Fires			Heading Fires		
PAH	0.5 kg/m^2	1.5 kg/m^2	2.4 kg/m^2	0.5 kg/m^2	1.5 kg/m^2	2.4 kg/m^2
Anthracene/phenanthrene	12,181	2,189	584	2,525	5,242	6,768
Methylanthracene	9,400	1,147	449	1,057	4,965	7,611
Fluoranthene	14,563	2,140	687	733	974	1,051
Pyrene	20,407	3,102	1,084	1,121	979	1,133
Methyl pyrene/fluoranthene	18,580	2,466	1,229	730	1,648	2,453
Benzo[c]phenanthrene	8,845	1,808	468	244	142	175
Chrysene/benz[a]anthracene	28,724	5,228	2,033	581	543	836
Methylchrysene	17,753	1,891	877	282	1,287	1,559
Benzofluoranthene	12,835	1,216	818	164	129	241
Benzo[a]pyrene	3,454	555	238	40	97	33
Benzo[e]pyrene	5,836	1,172	680	61	78	152
Perylene	2,128	198	134	33	24	46
Methylbenzopyrenes	6,582	963	384	65	198	665
Indenopyrene[1,2,3-cd]pyrene	4,282	655	169	-	-	-
Benzo[ghi]perylene	6,181	1,009	419	-	-	-
Total PAH	171,750	25,735	10,249	7,632	16,549	22,787

From U.S. EPA (1987). Data based on McMahon and Tsoukalas, 1978.

Fuel consumption is highly variable. On prescribed burn sites in Ontario, total fuel loadings of 0-15 kg/m^2 are considered light-moderate, and greater than 15 kg/m^2 as heavy. In general, the bulk of the fine fraction of this fuel will be consumed and this rarely exceeds 3.5 kg/m^2. Clearly, the bulk of the total fuel loading occurs in the heavy and duff fuels: in the former, the consumption levels range from 0.1 - 3.5 kg/m^2; in the latter, the consumption is 0.1 - 7.0 kg/m^2, depending on the duff type. The values are approximate (Ward, Ministry of Natural Resources, 1989).

Ontario data for the total coverage of wild and prescribed fires from 1984 to 1988 are presented in Table 3-29. There were an average 1,669 wild fires with an average coverage of 146,655 hectares and similarly, 44.4 prescribed fires covering an average of 9,714 hectares for the five year period.

The results from Tables 3-28 and 3-29 for emission factors and total yearly PAH emissions to the atmosphere from wild and prescribed fires in Ontario are summarized in Table 3-30.

3.3.6.3 Burning of Agricultural Waste

Prescribed burns also include the burning of waste consisting of leaves and slash, which has been referred to in the preceding chapter. For such burns the fuel loading can exceed 15 kg/m^2 and the typical emission factor is the same as for forest fires, Bjorseth and Ramdahl (1985). No data are available for prescribed burns conducted by farmers and householders.

TABLE 3-29

Wildfire and Prescribed Burn Occurrence in Ontario, 1984 to 1988

Year	Wildfires		Prescribed Burns	
	Number	Hectares	Number	Hectares
1988	3206	390,705	15	5,255
1987	1923	75,582	59	13,458
1986	1088	145,561	58	14,323
1985	887	1,007	43	10,635
1984	1240	120,420	47	4,901

Data from Ward, Ministry of Natural Resources, 1989.

TABLE 3-30

Average Yearly Emission Data for Polycyclic Aromatic Hydrocarbons from Wild and Prescribed Forest Fires in Ontario

PAH	Emission Factor (g/MT)	Coverage (ha/yr)	Total (MT/yr)
TSP	59,000-42,050*	156,369**	221,418-157,808
Total PAH	19.0 - 22.8* (20)	156,369**	71.4 - 85.5
Benzo[a]pyrene	0.033 - 0.095* (0.1)	156,369**	0.12 - 0.36

Notes:

* Range calculated for 100% head fires and 70%/30% head/back fires, with an average fuel loading of 2.4 kg/m^2

** five year average for wild and prescribed fires

() values in parenthesis from Bjorseth and Ramdahl, 1985

1976 estimated B[a]P production from wild forest fires in Ontario was 0.0075 MT/yr (Mellon et al., 1986).

Estimates for the total TSP, PAH and B[a]P emissions from wild and prescribed burns, including agricultural waste, have been included in Table 3-30.

3.3.6.4 Source Markers

Retene (1-methyl-7-ispropylphenanthrene) has been suggested as a source marker since it is produced as a result of the thermal transformation of resinous materials in wood, particulary softwood such as pine and spruce (Ramdahl et al., 1984). Similarly, it is claimed that the presence abietic acid, which is a precursor of retene, allows the distinction between smoke from a coniferous forest fire and smoke from grass or bush fires (Standley and Simonett, 1987). On the other hand, retene is also found in the ambient air as a result of coal combustion. Consequently, the recommended source-specific markers for forest fires are soil corrected potassium salts, carbon isotopes and beta levusan, Hornig et al. (1985).

3.4 Summary of PAH Emissions to the Atmosphere

A summary table of estimated total annual PAH emissions from some of the major sources to the atmosphere is provided (Table 3-31). These data are compared with estimated annual PAH emissions for the United States.

TABLE 3-31

Summary Table -
Atmospheric PAH Emissions

Source	Ontario PAH Emissions (MT/yr)	%	U.S. PAH Emissions* (MT/yr)	%
Industrial Production				
Coke Manufacturing	2 - 4	0.8	700	11
Petroleum Cracking	0.07 - 0.6	0.1	N.D.	-
Power Generation				
Coal-fired Plants	0.3	0.1	1	<0.1
Oil and gas boilers	1	0.3	-	-
Incineration				
Municipal Incineration	0.3 - 1.4	0.3	50	0.8
Mobile Sources				
Gasoline & Diesel Traffic	84.3	34	2,170	36
Natural Sources				
Forest Fires	71.4 - 85.5	32	1,000	17
Residential				
Oil and gas	1	0.3	-	-
Wood-burning (fireplaces & stoves)	65 - 90	32	700	12**
Total	260	100%	4,620	76%***

N.D. not determined

* From: Bjorseth and Ramdahl, 1985.
** This data includes coal burning in fireplaces and stoves.
*** Other industrial sources contribute the remainder.

4.0 TERRESTRIAL AND AQUATIC SOURCES AND INPUTS

4.1 Wet/Dry Deposition from the Atmosphere

Direct deposition from the atmosphere, both wet and dry, is probably the greatest source of PAH to soil and aquatic environments. Major sources to these media also include runoff, while municipal and industrial effluents also contribute to loadings to aquatic environments.

4.1.1 Plant Uptake

Plants may be exposed to PAH in the atmosphere and in soil, and thus may accumulate these compounds from either route. Considerable research has been carried out to determine PAH accumulation on leafy plant parts and by plants such as mosses which have a high bioaccumulation potential. Some information is available on PAH in plant material in Ontario, primarily from studies by Agriculture Canada on PAH occurrence in some food items.

The quantity of PAH accumulated by plants from the atmosphere is largely a function of the surface area to mass ratio of the plant parts considered. Thus, broad-leaved edible vegetables typically show the highest PAH concentrations (MOE, 1979; Grimmer, 1983). Thomas et al. (1984) measured concentrations of B[ghi]P, B[a]P, F and indeno[cd]perylene in a range of vegetation from an industrial area of Sweden, and found the highest concentrations in leaf litter, mosses and lichens (high surface area materials), and the lowest concentrations in conifer needles (low surface area materials). Thomas (1984) made concurrent measurements of PAH (1,12-benzoperylene, B[a]P, F) in atmospheric dust, precipitation and epiphytic mosses in Germany and used multiple regression to demonstrate that both dry deposition and wet deposition were important modes of PAH bioaccumulation.

Plants grown in an atmospheric concentration gradient of PAH have been found to accumulate PAH in proportion to the degree of contamination. Larsson (1985) measured the accumulation of 20 PAH in lettuce and rye grown at varying distances from a highway and found much greater concentrations in the lettuce than in rye, with decreasing concentrations occurring with distance from the road (Tables 4-1 and 4-2). In his review on PAH, Grimmer (1983) also reported that the PAH content of plant tissues depends on atmospheric PAH content.

The only Ontario study on PAH uptake by plants grown in a suspected pollution gradient showed plant tissues (grasses, pine needles, pear and apple leaves) were close to or below the detection limit for B[a]P and B[k]F based on 10 mg/MT dry weight (MOE, unpublished). The lack of any apparent PAH gradient or accumulation in this case can be attributed in part to the high detection limits relative to reported PAH concentrations in plant tissues in PAH-polluted environments (e.g., Thomas et al., 1984; Larsson, 1985).

Few studies have examined uptake and translocation of PAH from soils by plants and results of this research are inconclusive. Graf and Nowak (1986) reported root uptake of several PAH including B[a]P by tobacco, rye and radishes, while Harms (1975) reported negligible translocation of B[a]P from roots to shoots in wheat, and Gunther et al. (1976) reported no translocation of PAH into plant parts after application to the orange rind. Ellwardt (1977) reported little uptake of PAH from soils by several crops, while Durmishidze et al. (1974) observed translocations from leaves to roots and vice versa in several crops.

TABLE 4-1

Mean PAH Concentrations (mg/MT fresh weight) in Lettuce Grown at Various Distances from a Highway

	PAH Concentration (mg/MT) Distance from Highway					
PAH	8 m	15 m	25 m	35 m	45 m	65 m
PHEN	4.8	4.6	2.2	2.6	3.4	2.1
A	0.2	0.1	0.1	0.1	0.1	ND
2-MPHEN	1.6	1.5	0.6	1.0	0.8	0.6
MA	0.1	ND	ND	ND	ND	ND
1-MPHEN	1.8	1.4	0.7	1.0	0.8	0.7
F	7.1	5.5	3.2	4.1	3.6	3.8
P	8.6	7.0	4.2	4.6	4.5	3.8
B[a]FLN	2.4	1.2	0.7	0.7	0.4	0.2
B[b]FLN	3.3	0.9	ND	ND	ND	ND
1-MP	2.8	1.6	0.7	ND	ND	ND
B[a]A	1.7	1.3	0.9	0.7	0.6	0.4
CHR + TRI	5.1	3.6	2.6	2.5	1.9	1.6
BF's	3.5	2.3	1.6	1.4	1.6	1.3
B[e]P	1.6	1.2	0.9	0.6	0.6	0.6
B[a]P	0.8	0.4	0.5	0.4	0.3	0.3
PER	0.1	0.1	0.1	0.1	ND	ND
IN[1,2,3-cd]P	0.7	0.5	0.4	0.4	0.1	0.3
DBAs	ND	ND	ND	ND	ND	ND
B[ghi]PER	1.7	1.1	0.9	0.9	0.8	0.7
ANTHN	ND	ND	ND	ND	ND	ND
Total PAH	46	34	22	22	20	16

ND - not detected

From: Larsson, 1985.

TABLE 4-2

Mean PAH Concentrations (mg/MT fresh weight) in Whole Rye Grains Grown at Various Distances from a Highway

	PAH Concentration (mg/MT) Distance from Highway		
PAH	7 m	15 m	25 m
PHEN	1.5	1.3	1.4
2-MPHEN	0.7	0.5	0.6
1-MPHEN	0.3	0.3	0.3
F	1.3	1.0	0.9
P	2.3	1.8	1.6
B[a]A	0.2	ND	ND
CHR + TRI	0.7	0.4	0.3
BFLN	0.2	0.2	ND
B[e]P	ND	0.1	ND
Total PAH	7.5	6.0	5.7

ND - not detected.

From: Larsson, 1985.

Edwards et al. (1982) reported uptake and translocation of radio-labelled anthracene from nutrient solution, with the degree of uptake proportional to concentration in solution. Using radio-labelled A and B[a]A, Edwards (1985) reported rapid assimilation and retention from solution in bush bean roots, with assimilation varying directly with PAH level in solution and rapid translocation of PAH metabolites in the plant. In the latter study, bioconcentration factors for the parent compound were reported as 4,613 and 2,515 for B[a]A and A in roots, respectively. No accumulation of B[a]A occurred in stems, although some accumulation of A in stems was noted (bioconcentration factor of 1.9). Using soils spiked with PAH (B[a]P, B[b]F, B[k]F and DB[a,h]A), Wegmann et al. (1987) also found that PAH accumulated from soil was retained mainly by root tissues, with the degree of accumulation depending on exposure concentration. Overcash et al. (1986) measured bioaccumulation of B[a]A, A and PHEN by corn, wheat, fescue and soybean grown in soils containing PAH concentrations of 0, 0.1, 1.00 and 10.0 ppm. Linear regression equations were developed that predicted uptake of PAH from soil under the experimental conditions imposed. Equations for corn, wheat seed and soybean seed are presented in Table 4-3.

The degree of uptake consistently occurred in the order A > B[a]A > PHEN, suggesting that smaller molecules are accumulated more readily than larger molecules. Based on the most recent of these studies, it may be concluded that PAH are accumulated via root uptake and that root tissues may be expected to accumulate the highest PAH concentrations.

TABLE 4-3

Regression Equations for Plant Uptake of Polynuclear Aromatic Hydrocarbons

Plant	PAH	Regression Equation
Corn	Anthracene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = 0.108 + 1.137\ [\log_{10}(\text{rate} + 1)]$ r^2 (correlation coefficient) = 0.95
Soybean Seed	Anthracene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = 0.136 + 0.018 \log_{10}(\text{rate})$ $r^2 = 0.94$
Wheat Seed	Anthracene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = -0.044 + 0.012 \log_{10}(\text{rate})$ $r^2 = 0.99$
Corn	Benz[a]anthracene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = -0.164 + 1.056 \log_{10}(\text{rate})$ $r^2 = 0.95$
Soybean Seed	Benz[a]anthracene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = -0.019 + 0.008 \log_{10}(\text{rate})$ $r^2 = 0.85$
Wheat Seed	Benz[a]anthracene	rate is not significant
Corn	Phenanthrene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = 0.054 + 0.008 \log_{10}(\text{rate})$ $r^2 = 0.97$
Soybean Seed	Phenanthrene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = -0.082 + 0.319\ [\log_{10}(\text{rate} + 1)]$ $r^2 = 0.90$
Wheat Seed	Phenanthrene	$\text{Log}_{10}[\text{dw(ppb)} + 1] = 0.016 + 0.004 \log_{10}(\text{rate})$ $r^2 = 0.98$

dw (ppb) - dry weight in ppb in plant/seed
"rate" as PAH concentration in soil (ppm). Note: this is a concentration term.

From: Overcash et al., 1986.

4.1.2 Biosynthesis

Evidence for the biosynthesis of PAH compounds by organisms is inconclusive. Some organisms, including certain bacteria, fungi, plants and some animals, have been shown to synthesize a variety of polycyclic quinone pigments (Thompson, 1971), which may be transformed to PAH compounds by diagenesis in the open environment (NRCC, 1983).

Neff (1979) and Harms (1975) examined evidence both for and against complete biosynthesis of PAH. In some cases of reported biosynthesis, contamination by PAH external to the experimental system could not be dismissed (NRCC, 1983). While there appears to be a general acceptance that some limited biosynthesis of PAH by microorganisms may occur under certain environmental conditions, there is also agreement that its significance in the overall PAH budget is very low (Harms, 1975; Suess, 1976; Grimmer, 1983; Matzner, 1984). On this basis, it may be concluded that biosynthesis is an insignificant source of PAH in soils and other natural media in Ontario.

4.1.3 Diagenesis

PAH are formed naturally during carbonization processes, such as coal and mineral oil formation. Low temperatures (typically less than 150 to 200°C) favour the formation of alkylated PAH slowly in these deposits over periods of millions of years (Youngblood and Blumer, 1975; Grimmer, 1983). PAH precursors are slowly transformed into extensively alkylated and cylcloalkylated forms and unalkylated PAH occur only in low abundances in these deposits (Blumer and Youngblood, 1975). Thus, fossil fuels tend to show high ratios of alkylated to unalkylated forms.

In diagenically-formed PAH, the PAH profiles typically show marked differences from those formed during combustion (Grimmer, 1983). For example, in mineral oil, B[e]P is the predominant benzopyrene, while B[a]P is not abundant; conversely, in oil or gasoline combustion products, the ratio of these isomers is about 1:1. Phenanthrene is about 50 times more abundant than anthracene in mineral oil, while the P:A ratio in automotive combustion gases is about 4:1.

PAH may also form in marine and lake sediments. The molecular weights and composition of PAH in these mixtures are affected by the source of PAH precursors and by the depositional environment (Aizenshtaf, 1973). For instance, Maxwell et al. (1971) reported that PAH may form in anoxic sediments through dehydrogenation, dehydroxylation and aromatization of polyhydroxy-quinone pigments. Conversion of carotenoid pigments from marine sediments to PAH under low temperatures (65 to 200°C) has been observed over short time frames (two months) (Ikan et al., 1975). Other diagenetic pathways for specific PAH are noted in a recent review NRCC (1983).

The role of diagenesis of PAH in the overall budget of PAH in the open environment remains unresolved. Diagenesis has occurred over geologic time scales in Ontario in oil deposits, such as in southwestern Ontario and probably occurs over shorter periods in lake sediments. The diagenesis of PAH in soils has apparently not been reported; although, as in lake sediments, the formation of PAH in soils under certain conditions cannot be discounted.

4.1.4 Wood Preservation

There are 17 wood preserving plants in Ontario, six of which use organic wood preservatives (Beak, 1987). Of these six, three use creosote, which typically contains high concentrations of PAH. PAH are also found in fuel oils that are usually used a solvents for facilities that use only pentachlorophenol (PCP) as the preserving agent (U.S. EPA, 1986), although creosote probably represents a greater potential source of PAH to the environment than do PCP solvents.

Creosote is a distillate of coal tar used extensively in wood preservation. There are three wood preserving plants in Ontario that use creosote - one at Thunder Bay, one at Trenton and one at Newcastle (presently closed). An estimated 20,000 tonnes of creosote are used annually by the ten wood preserving plants in Canada (K. McKellar, Department of Regional Industrial Expansion, pers. comm.). Based on the number of wood preservers in Ontario and in Canada, an estimated 20 to 30% of the total creosote usage, or 4,000 to 6,000 tonnes, takes place in Ontario.

The detailed composition of creosote used in Canada has apparently never been determined (Ralph, C., Agriculture Canada, pers. comm.), although Uthe (1979) provided data on creosote, coal tar and wood preservative sludges (Table 4-4).

Berard and Tseng (1986) reported PAH concentrations in surface soils and groundwater at the Northern Wood Preservers plant in Thunder Bay, as shown in Tables 4-5 and 4-6. This PAH contamination of the soil and groundwater at the site can probably be attributed to routine operational spillage and losses from storage areas.

TABLE 4-4

PAH Content of Creosote, Creosote Sludge and Coal Tar

Compound	Creosote	Creosote	Creosote Sludge	Coal Tar	Wood Preservation Sludge
Anthracene	43	18	-	-	-
Benz[a]anthracene	-	-	31	43 (2)	5
Benzo[b]chrysene	-	-	-	23 (4)	5
Benzo[j]fluoranthene	-	-	-	1	0.3
Benzo[k]fluoranthene	-	-	-	33	7
Benzo[ghi]perylene	-	-	-	18 (5)	-
Benzo[a]pyrene	-	13	-	33	3.6
Chrysene	-	-	-	-	2.5
Fluoranthene	5.5	-	70	-	5 (3)
Perylene	-	-	-	54	26
Phenanthrene	186	125	193	3	-
Pyrene	2.6	-	64	81 (1)	15 (1)
Acenaphthene	60	70	67	47	24
Fluorene	103	53	48	-	-
2-Methylanthracene	9.8	-	-	27	6
9-Methylanthracene	2.4	-	-	-	8
Benzofluorene	1.2	-	-	-	-

(1) Phenanthrene and anthracene.
(2) Contains chrysene, triphenylene and all benzanthracenes.
(3) Contains chrysene and triphenylene.
(4) Contains benzo[a]chrysene and phenylenepyrene.
(5) Contains benzo[ghi]perylene and anthanthrene.

From: Uthe, 1979.

TABLE 4-5

Northern Wood Preservers Survey

Soil and Sediment
Extractable Organics by GC/MS

	Concentration ug/g dry weight
Acenaphthene	117
Acenaphthylene	6
Anthracene	53
Phenanthrene	1292
Benz[a]anthracene/chrysene	164
Benzo[b & k]fluoranthene	71
Fluoranthene	378
Fluorene	213
Pyrene	242
Benzo[a]pyrene	-
Carbazole	40
Quinoline	69

- not detected

From: Berard & Tseng, 1986.

TABLE 4-6

Northern Wood Preservers Survey

Groundwater
Extractable Organics by GC/MS

	Well #7 (ug/L)	Well #8 (ug/L)	Well #12 (ug/L)	Well #15 (ug/L)
Acenaphthene	<5		<70	12
Anthracene	<3			<2
Fluoranthene	17	<5		<4
Pyrene	8	<5		

No phenanthrene, benz[a]anthracene, chrysene, benzo[b&k]fluoranthene, fluorene, acenaphthylene or quinoline were detected.

From: Berard & Tseng, 1986.

These contaminated soils and groundwaters may be expected to result in some locally significant PAH loadings into nearby surface waters, through erosion and groundwater flow. The Ministry of the Environment has now issued a Control Order to Northern Wood preservers for clean up of PAH contamination in Thunder Bay Harbour. Information on sludge generation and PAH levels at other major wood preserving facilities in Ontario is not readily available.

4.1.5 Sewage Sludge Disposal

Disposal of sludges generated in sewage treatment poses a disposal problem that is generally addressed through incineration or land disposal in Ontario. Open water disposal of sludges is not practiced in Ontario. Incineration of sludges is expensive in terms of energy consumption, but achieves substantial reductions in volume and thereby facilitates disposal.

Use of sewage sludge as a fertilizer on farmland is becoming an increasingly attractive disposal option and is widely practiced in Ontario following the Ontario Ministries of Agriculture and Food, Environment and Health guidelines for sludge utilization (OMAF/OME/OMH, 1986). Approximately 1.25 x 10^6 m^3 of wet sludge, or nearly 20% of the 6.5 to 7 x 10^6 m^3 of sludge generated annually in Ontario, is spread on agricultural land (F. Iliffe, OME, pers. comm.).

PAH levels in sewage sludge depend on loadings into sewage treatment systems and on system performance. PAH in Ontario sewage systems were recently investigated in a survey of 37 water pollution control treatment plants under the provincial Municipal/Industrial Strategy for Abatement (MISA) program (Environment Ontario, 1988). A summary of these data is presented in Tables 4-7 and 4-8.

TABLE 4-7

Summary of MISA PAH Data for 37 Ontario Water Pollution Control Plants

PAH	Raw Sewage	Primary	Geometric Mean Concentration* (ug/L) Secondary	Tertiary	Lagoon	Geometric Mean Concentration (ug/kg) Raw Sludge	Treated Sludge
Acenaphthylene	-	-	-	-	-	4406.7	1909.4
Anthracene	-	-	-	-	-	2919.8	1306.9
Benz[a]anthracene	5.03	-	1.08	1.29	1.08	-	1379.5
Benzo[a]pyrene	-	-	-	-	-	-	1333.3
Benzo[b]fluoranthene	5.01	-	-	-	-	2424.2	-
Benzo[k]fluoranthene	5.03	-	1.07	1.16	-	-	1350.2
Chrysene	-	-	-	-	-	3206.9	1475.5
Fluoranthene	5.09	-	-	-	-	3083.5	1335.9
Fluorene	5.02	1.05	-	-	-	-	1352.1
Phenanthrene	5.17	-	1.07	-	-	3563.5	2220.5
Pyrene	7.51	-	1.61	1.85	-	4522.1	2124.3
Total PAH	37.9	1.05	4.8	4.3	1.09	24,447	15,787

From: Environment Ontario, 1988.

TABLE 4-8

Summary of Ontario Water Pollution Control Plants Tested, Flow Rates, PAH Concentrations and Estimated PAH Emission Rates

Test Plants	Average Flow Rate (10^3 kL/day)	PAH Concentration (ug/L)	Estimated Emission Rate (kg/yr)
Guelph	43.4	4.3	68.1
Secondary Plants		4.8	
Belle River	5.6		9.8
Brantford	52.1		91.3
Burlington	67.0		117.4
Grimsby	13.1		23
Hamilton	306.5		537
Kingston	18.0		31.5
Kitchener	70.6		123.7
London (Greenway)	110.8		194
London (Potterburg)	16.3		28.6
Mississauga (Clarkson)	74.7		130.9
Mississauga (Lakeview)	256.9		450
Moore	2.2		3.9
Niagara Falls	58.2*		102
Oakville	13.5		23.6
Paris	2.5		4.4
Peterborough	50.8		89
Pickering	176		308
Sault Ste. Marie	6.65		11.7
Sudbury	49		85.8
Toronto (Highland Creek)	170		298
Toronto (Humber)	403		706
Toronto (Main)	767		1,344
Toronto (North)	36.6		64.1
Waterloo	46.4		81.3
Wallaceburg	6.8		11.9
Whitby	3.6		6.3
Windsor	32.8		57.5

* Design flow rate: actual flow rate was not recorded.

From: Environment Ontario, 1988.

TABLE 4-8 (cont'd)

Summary of Ontario Water Pollution Control Plants Tested, Flow Rates, PAH Concentrations and Estimated PAH Emission Rates

Test Plants	Average Flow Rate (10^3 kL/day)	PAH Concentration (ug/L)	Estimated Emission Rate (kg/yr)
Primary Plants		7.05	
Cornwall	43.7		16.7
Kingston (City)	63.5		24.3
Ottawa	400		153
Sarnia	54		20.7
Sault Ste. Marie (East)	32		12.3
Thunder Bay	81		31
Windsor (Westerly)	123.6		47.4
Lagoons		1.08	
Lindsay	14.2		5.6
Niagara-on-the-Lake	6.4		2.5
Total	3,678.5		5,316.3

* Design flow rate: actual flow rate was not recorded.

From: Environment Ontario, 1988.

The estimated annual PAH emission from the 37 plants for 1987 was 5,316 kg (Table 4-8). The estimated total flow from these plants was 3,678,000 kL/day or 73.6% of the total Ontario flow from the 412 municipal treatment facilities for the same year. A rough estimate of the total annual PAH loading from these facilities is 5,316/0.736 = 7.2 MT.

Zukovs et al. (1984) provided quantitative data on PAH partitioning in aqueous and solid phases of Hamilton sewage, but did not analyze PAH in the digested sludges. PAH concentrations were, however, measured in primary treatment solids and in waste activated sludge, which would subsequently pass through further treatment (digestion and possibly dewatering) followed by disposal (incineration at Hamilton, land-base disposal at many other plants). Data on total PAH loadings to the plant in raw sewage and to Hamilton Harbour in treated sewage are available (Table 4-9). Assuming no biodegradation of PAH in the sewage plant, the difference between the influent and effluent loadings in Table 4-9 would represent PAH loadings into the solids disposal pathway.

Unpublished data from Grimmer (cited in Grimmer, 1983) and an earlier study by Borneff and Kunte (1967) show no evidence for biodegradation of PAH in a European sewage plant, although effective biodegradation has been demonstrated in soil systems (Bulman et al., 1985).

Webber and Lesage (1987) analyzed PAH in sewage sludges from several Canadian cities. These sludges were thought to represent worst-case sludges in terms of contamination by organics, because they were obtained from industrial centres. A summary of their data, in terms of concentration ranges and frequencies of occurrence, and a comparison with sludges from the U.S. are summarized in Table 4-10.

TABLE 4-9

Loadings of PAH to the Hamilton Sewage Treatment Plant in Raw Sewage and from the Plant in Treated Effluent

	Trace Organics*	
Contaminant	In (kg/yr)	Out (kg/yr)
Acenaphthylene	613	4.1
Fluorene	1,526	19.0
Fluoranthene	4,066	65.7
Carbazole	2,310	43.8
Pyrene	3,705	84.0
Benzo[a]pyrene	4,420	69.4

* These estimates are based on average values from 14 sampling days, and include very high values measured on one or two days for most contaminants. Thus, these annual averages are considered to be high estimates.

From: Zukovs et al., 1984.

TABLE 4-10

Summary of Canadian and International Data on PAH in Municipal Sewage Sludge[1]

	Hamilton Dec. 1981-Jan. 1982 Concentration	15 Canadian Sludges[2] Occurrence Concentration			40 U.S.A. Sludges Occurrence Concentration	
Compound	Range	%	Range	Median	%	Range
Acenaphthene	4-6	33	t-<3	t	5	<1-115
Acenaphthylene	42-47	27	t-5	t	1	<1-8
Anthracene	141-599	20	t-32	1	48	<1-250
Phenanthrene		53	t-36	2	53	<1-250
Benz[a]anthracene		7	<0.5		27	<1-38
Chrysene	39-60[3]	27	t-23	1.5	31	<1-38
Benzo[b]fluoranthene		7	0.5			
Benzo[k[fluoranthene	40-43[4]	13	0.5-9	5		
Benzo[ghi]perylene	t-42	13	t-0.3	0.2		
Benzo[a]pyrene	28-34	13	4-7.2	5.6	5	<1-12
Benzo[e]pyrene						
Dibenzo[a,h]anthracene		7	13			
Fluoranthene	232-334	53	t-33	2	44	<1-250
Fluorene	98-115	60	t-3	2	6	1-32
Indeno[1,2,3-cd]pyrene	t-38	7	7		2	<1-2
Naphthalene	23-45	60	t-5.8	1	34	<1-130
Pyrene	171-236	67	t-29	3.5	53	<1-43

t trace
1 all concentrations in mg/g dry sludge
2 excluding data on Hamilton sludges prior to October 1983
3 Benz[a]anthracene and chrysene combined
4 Benzo[b]fluoranthene and benzo[k]fluroanthene combined

From: Webber and Lesage, 1987.

They also concluded that PAH concentrations were highest in Hamilton among Canadian sludges, apparently due to the local steel industry, but that differences in PAH concentrations among other sludges were relatively small. Higher PAH concentrations were reported for PAH in Hamilton prior to the onset of the economic recession in 1982, possibly due to a reduction in industrial activity (Table 4-10).

The average solids content of wet sludge, as it is landspread, is about 3.5%. If PAH concentrations in Ontario sewage sludges are similar to those reported by Webber and Lesage (1987), then an average PAH profile for wet sludge in Ontario could be constructed. For example, the average B[a]P content of dried Canadian sludge is 5.6 mg/kg and 1.3 mg/kg for Ontario treated sludge (from Tables 4-7 and 4-10), which is equivalent to 0.05-0.2 mg/L on a wet sludge basis. In the 6.5 to 7 million cubic metres of sludge generated in the province, there would be an estimated 337 to 1350 kg of B[a]P, of which about 60-250 kg would be applied to farmland; the remainder being incinerated or disposed of in landfills. Application rates to farmland, following the OMAF/OME/OMH (1986) application guideline of 135 kg of ammonium plus nitrate nitrogen per hectare per five-year period, assuming a typical nitrogen content of about 500 ppm for digested sludge, would thus be about 13-54 $g \cdot ha^{-1}$ of B[a]P over five years.

4.1.6 Disposal of Oil Refinery Sludges

Oil refinery sludges have been treated in a variety of ways in the past. Landspreading of oil sludges has been practiced since the 1950s, but came into common practice only more recently. Alternatives to landspreading including landfilling, incineration, lagooning and solidification. Landspreading of petroleum sludged is practiced to immobilize the sludge mass within the upper soil layers and to allow biodegradation of hydrocarbons while preventing releases of harmful vapours, runoff and leachate (Brown et al., 1980).

To maximize biodegradation, treated soils are frequently tilled to maintain aerobic conditions. Fertilizers are also applied in many cases. Sites used for landspreading are typically owned or controlled by the refineries generating the oily wastes and are not used for other purposes. Reviews of landspreading practices for oil sludges are provided by Beak (1981) and Canviro (1983).

Various types of refinery sludges are generated at Canadian facilities. PACE (1980) identified 10 categories for Canadian oil refinery sludges: desalting sludge, A.P.I. sludge, flotation froth, biosludge, basin settlings, storm silt, filter backwash, slop emulsions, cooling water tower sludge and unleaded tank bottom sludge. These sludges vary greatly in composition, from those containing very low hydrocarbon contents, to those with high hydrocarbon contents.

Rates of refinery sludge application onto soils vary with site conditions (soil characteristics, climate, etc.). CONCAWE (1980) suggested a maximum rate of application of oily constituents of 15 kg/m^2, subject to site limitations. Beak (1981) noted that reapplication is normally practiced only when the oil content in the surface soil has decreased to 1-4%. Data on overall loadings of oily sludges in refinery landfarms in Ontario or Canada have apparently not been compiled, although limited data on individual refineries were provided in the Beak (1981) report, showing limited data on individual refineries and showing typical total annual rates of a few hundreds to a few thousands of tonnes of sludges per year per refinery. Among Canadian refineries, landspreading is the second-most important disposal method (on a dry weight basis) for refinery wastes, with landfill disposal being the most important PACE (1980).

PAH concentrations in oil refinery waste sludges were determined by Can Test (1982). More recent analyses of PAH levels in sludges from a Canadian refinery having the "best practicable treatment technology" were undertaken by Beak (1985). Data from these sources are presented in Tables 4-11. Loadings of some PAH to landfarms could be roughly estimated using the limited available data. Data on losses of PAH to the open environment from landfarms through leachate, runoff or volatilization, are unknown.

4.1.7 Coal Gasification Wastes

Intera Technologies Limited (1987) conducted a historical survey and site reconnaissance of coal gasification solid waste disposal sites in Ontario and identified 41 sites in 36 different municipalities province-wide. These wastes were generated through the manufacture of gas from coal or oil over the period of about 1850 to 1950 for use in street lights, appliances, furnaces and industrial engines. Sludges, tars and other solid wastes from these operations are rich in PAH; coal tar may consist of up to 3% of PAH by weight (Grimmer, 1985).

Many of these waste sites have been identified as presenting a high potential for release of waste constituents into the local environment. Data on PAH from the site identified at Port Stanley (D. Veal, OME, pers. comm.) show that PAH are leaking from the buried coal gas waste through the local groundwater system and into the local surface water environment (Kettle Creek).

TABLE 4-11

Concentrations of Base-Neutral Organics in Oil Refinery Disposal Sludges

Base Neutral Organics, ug/g, dry wt.

Acenaphthene	ND	Trace
Acenapthylene	ND	ND
Anthracene	Trace	Trace
2-Methyl Anthracene	Trace	20.2
Benz[a]anthracene	ND	ND
Benzo[k]fluoranthene	ND	ND
Benzo[a]pyrene	ND	ND
Chrysene	19.3	20.8
Fluoranthene	ND	ND
Fluorene	ND	Trace
Phenanthrene	Trace	Trace
Pyrene	ND	Trace

ND - not detected

From: Beak, 1985.

Similar wastes at Sydney, Nova Scotia are the subject of intense study by Environment Canada, owing to high rates of contaminant release into the marine environment. The importance of these buried wastes as a PAH source to local groundwaters and other environments is yet unknown, although the potential significance of some of these wastes as major local PAH sources in Ontario should not be discounted.

4.2 Direct Deposition (Wet/Dry) from the Atmosphere to Aquatic Systems

The identification of PAH in sediments and aquatic biota has led many authors to speculate that the atmosphere deposition of PAH-containing particles to surface waters and adjacent watersheds is a significant route of entry for these compounds into the aquatic environment and may be responsible for much of the background concentration in the absence of other identifiable sources (NRCC, 1983). Direct atmospheric input appears to be the major source of PAH to the Great Lakes (Eadie, 1984).

In Lake Michigan, concentrations of total PAH in the surface microlayer varied from 0.15 to 0.45 ug/L, which represented approximately 10^6 times the atmospheric concentration (Strand and Andren, 1980). Analysis of the surface film of water from the Detroit River showed PAH concentrations were often 10^2 to 10^4 above subsurface water samples (Comba et al., 1985). These results support the suggestion that aerosols are a major source of PAH and indicate that the microlayer is a repository until PAH are removed by adsorption and sedimentation (Strand and Andren, 1980).

4.2.1 Rainfall as a PAH Source

Trace organics such as PAH exist in the atmosphere in both the vapour phase and adsorbed to particulate matter. Since atmospheric fluxes of contaminants to water are a combination of dry and wet deposition processes, reliable data on vapour and particle-associated concentrations are required to estimate these fluxes. Unfortunately, atmospheric sampling methods are inadequate to differentiate between vapour and aerosol PAH. Estimation of deposition rates to Ontario must rely on incorporation of data from world-wide studies. It is expected however, that wet deposition of praticle-bound PAH would dominate (Ryan and Cohen, 1986; Mackay et al., 1986).

Eisenreich et al. (1981) reported much lower PAH concentrations for precipitation in the Great Lakes basin, with concentration ranges between 0.1 and 4.5 ng/L for individual compounds (anthracene, phenanthrene, pyrene, benzo[a]anthracene, perylene and benzo[a]pyrene). The dominant PAH in rain and snow samples in urban and rural samples from southern California were PHEN, F and P with total PAH concentrations reported as 17 to 261 ng/L for urban samples, and 27 to 80 ng/L for rural samples (Kawamura and Kaplan, 1986).

In Rotterdam, van Noort and Wondergen (1985) reported PHEN, F, B[a]A, B[b]F, B[a]P, DB[a,h]A, B[ghi]PER and IN[1,2,3-cd]P as the dominant PAH in rainfall at 7 to 180 ng/L each, with P and CHR detected only sporadically. In the Rotterdam study, it was found that the instantaneous rate of deposition declined with the quantity of precipitation, and removal rate constants on a precipitation amount basis were 1.46 to 3 mm^{-1}. Deposition rates to the ground surface (and thus to soils or runoff) for one event were 11.5 to 124.5 ng/m^2.mm for individual PAH during a for one event were 11.5 to 124.5 ng/m^2.mm for individual PAH during a single precipitation event (Table 4-12).

Ligocki et al. (1985a,b) reported dissolved and particulate concentrations of several PAH in Portland, Oregon rainfall (Table 4-13), and in ambient air, and found that, for most PAH, particle scavenging was less important than gas scavenging during precipitation events. Limited data on PAH in precipitation samples from Sarnia and Windsor show high concentrations of PHEN, P and F (700 to 900 ng/L) at some locations.

Rates of dry deposition for PAH are generally unavailable, but are included in measurements of bulk deposition onto terrestrial environments. Bulk deposition rates appear to be unavailable for Ontario. In rural, forested areas of West Germany, Matzner (1984) measured annual deposition rates of B[a]P, 1,12-benzoperylene, IN[1,2,3-cd]P and F through canopy drip, stemflow and litterfall, and reported that accumulation rates of 385 to 2,720 mg$\cdot$ha$^{-1}\cdot$yr^{-1} (Table 4-14). Much of the PAH flux to the soil was transferred by litterfall, indicating adsorption of PAH on leaf surfaces.

Harrison et al., (1985) measured deposition rates of six PAH at varying distances from a highway, and reported rates of about 11 ug$\cdot$m^{-2} for F, 7 ug$\cdot$m$^{-2}\cdot$wk^{-1} for B[b]F, and 2 to 5 ug$\cdot$m$^{-2}\cdot$wk^{-1} for A, B[a]A, B[k]F and B[a]P. Most of the PAH was deposited within 15 m of the roadway, and background deposition rates (less than 1 ug$\cdot$m$^{-2}\cdot$wk^{-1}) were found at greater distances. For reference purposes, it is noted that measurements of soil concentrations near a highway in the U.K. indicated measureable PAH fallout from traffic to a distance of at least 100 m from the highway (Butler et al., 1984).

TABLE 4-12

Data for the Correlation Between PAH Deposited and the Amount of Rain

Compound	Correlation Coefficient r^2	PAH Concentration/ Amount of Rainfall Ratio ng/(m^2mm)
Phenanthrene	1.000	89.2
Fluorene	0.9987	124.5
Benz[a]anthracene	0.9819	21.8
Benzo[b]fluorene	0.9985	65.5
Benzo[k]fluorene	0.9980	27.9
Benzo[a]pyrene	0.9933	27.3
Dibenz[a,h]anthracene	0.9912	11.5
Benzo[ghi]perylene	0.9962	62.2
Indeno[1,2,3-cd]pyrene	0.9955	89.8

From: Van Noort & Wondergen, 1985.

TABLE 4-13

Particle-Bound and Dissolved PAH Concentrations in Rainfall Collected in a Residential Area of Portland, Oregon

Compound	Particle-Bound PAH Concentration (ng/L)	Dissolved PAH Concentration (ug/L)
Acenaphthene	-	5.4
Acenaphthylene	-	24
Fluoranthene	0.44	14
Phenanthrene	4.1	90
Anthracene	-	5.1
Methylphenanthrene	3.3	30
Fluorene	4.4	48
Pyrene	4.1	39
Benz[a]anthracene	1.5	3.3
Chrysene	3.6	7.8
Benzo[e]pyrene	3.0	<0.37
Benzo[a]pyrene	2.8	<0.18
Perylene	0.58	-
Coronene	3.3	-

Means of 7 samples.
From Ligocki et al., (1985a,b)

TABLE 4-14

Annual Rates of Total Deposition of PAH in Forest Ecosystems

	Deposition Rate ($mg\ ha^{-1} yr^{-1}$) Spruce		Beech	
Indeno[1,2,3-cd]pyrene				
Canopy drip	412	± 40	426	±110
Stemflow	0		60	
Litterfall	470	± 50	230	± 30
Total deposition	882	± 64	716	±118
Benzo[ghi]perylene				
Canopy drip	663	±140	524	± 60
Stemflow	0		80	
Litterfall	520	± 80	240	± 30
Total deposition	1183	±160	844	± 67
Fluoranthene				
Canopy drip	880	±130	580	±100
Stemflow	0		90	
Litterfall	1840	±200	710	± 70
Total deposition	2720	±240	1380	±120

From: Matzner, 1984.

Background deposition rates of 29 to 71 $ug{\cdot}m^{-2}{\cdot}yr^{-1}$ for total PAH in the Harrison et al., (1985) study were slightly below background deposition rates of 100 to 170 $ug{\cdot}m^{-2}{\cdot}yr^{-1}$ reported by Quaghebeur et al. (1983) in Belgium, and considerably lower than the approximately 330 to 560 $ug{\cdot}m^{-2}{\cdot}yr^{-1}$ measured for four PAH by Matzner (1984) in forested German ecosystems. Assuming an average atmospheric deposition rate of 100 $ug.m^{-2}.yr^{-1}$ for the Ontario landmass (916,734 km^2), the estimated PAH loading in 91.7 MT/yr.

Eisenreich et al. (1981) used information from a variety of sources to estimate total PAH deposition to the Great Lakes (Table 4-15). The total flux of PAH (A, Phen, P, B[a]A, Per, B[a]P) to all the lakes was estimated to be 484 tonnes per year. Due to the proximity of much of Ontario's population and atmospheric PAH sources to the Great Lakes, the estimated aerial fluxes of each compound may not be representative of most of the Ontario land mass. Deposition rates are much greater near their sources (urban centres, highways, etc.) (Kawamura and Kaplan, 1986; Harrison and Johnston, 1985; Butler et al., 1984).

Based on core profiles and estimated deposition rates, PAH fluxes to sediments in the northeastern United States were estimated for various time periods during the 20th century (Gschwend and Hites, 1981; Hites and Gschwend, 1982). PAH deposition rates were clearly higher near urban centres, but the proportions of PAH derived from the atmosphere were not compared with water-based inputs (Table 4-16).

Since PAH input to the Great Lakes area is thought to be predominantly from atmospheric sources (Eadie, 1984), it is assumed that the sediment deposition rates will reflect these atmospheric deposition trends.

TABLE 4-15

Total Deposition of PAH to the Great Lakes

Compound	Deposition Rate (MT/yr) Superior	Michigan	Huron	Erie	Ontario	Total
Total PAH	163	114	118	51	38	484
Anthracene	4.8	3.4	3.5	1.5	1.1	14.3
Phenanthrene	4.8	3.4	3.5	1.5	1.1	14.3
Pyrene	8.3	5.9	6.1	2.6	1.9	24.8
Benz[a]anthracene	4.1	2.9	3.0	1.5	1.1	12.6
Perylene	4.8	3.3	3.4	1.5	1.1	14.1
Benzo[a]pyrene	7.9	5.6	5.8	2.5	1.8	23.6

Deposition based on PAH concentration in air as reported in the literature.

From: Eisenreich et al., 1981.

TABLE 4-16

PAH Fluxes to Sediments from 5 Remote Sites in the Northeastern United States and 3 Urban Sites PAH Flux (ng.cm^{-2}y^{-1})

Site	Time Interval	PAH Flux (ng·cm^{-2} y^{-1})							
		Phen-anthrene	Anthra-cene	Fluor-anthene	Pyrene	Benz[a]-anthracene	Chrysene/Tripheny-lene	B[e]P	B[a]P
REMOTE SITES									
Lake Superior	1955-1980	0.3	0.03	1	0.6	0.3	1	0.9	0.4
Isle Royale, Lake Superior	1974-1980	0.4	0.01	0.4	0.3	0.2	0.8	0.8	0.2
Sommes Sound, Mount Desert Island, Maine	1960-1980	2	0.2	5	4	2	2	2	2
Hadlock Lower Pond, Mount Desert Island, Maine	1950-1980	2	0.1	4	3	0.6	1	0.8	0.6
Coburn Mountain Pond, Maine	1975-1980	2	0.2	4	3	0.7	2	2	0.7
Averages	current (1980)	1	0.1	3	2	0.8	1.5	1.5	0.8
URBAN SITES (Massachussetts)									

From: Gschwend & Hites, 1981; 1982.

Atmospheric deposition is thought to be the source of PAH found in remote aquatic environments, so demonstrated by Gschwend and Hites (1981) and Bailey and Howell (1983). Indeed, the chronology of atmospheric PAH contamination appears to be preserved in the sediments of remote lakes (Gschwend and Hites, 1981).

Very little data on PAH concentrations in precipitation have been collected in Ontario. Preliminary data on PAH in rainwater in Sarnia and Windsor (industrial areas) were provided by J. Marsalek of the National Water Research Institute (pers. comm.), as shown in Table 4-17. These data may be used to estimate wet depositional fluxes of some PAH at these locations. The current Ontario MOE Air Resources Branch 6-site network for measuring wet deposition and airborne concentrations of organics, including PAH will soon address this deficiency.

It has been assumed that the only major sources of PAH to aquatic environments in rural Ontario are atmospheric. Background deposition rates are not yet available for Ontario and no Canadian data were found. A study conducted on the west coat of the U.K. indicated background bulk deposition of A, F, B[a]A, B[a]F, B[k]F and B[a]P was about 30 ug/m^2/yr (Harrison and Johnston, 1985). Another European study conducted in inland Belgium resulted in higher flux background rates of approximately 100 to 170 ug/m^2 PAH/year (F, B[b]F, B[k]F, B[a]P, B[ghi]Per and In[1,2,3-cd]P (Quaghebeur et al., 1983). Assuming an average PAH deposition rate to surface water within the land boundaries for Ontario of 100 ug/m^2/yr, the loading to inland waters (177,390 km^2) is 17.7 MT/yr in comparison with the loading of 484 MT/yr to the Great Lakes.

TABLE 4-17

PAH-Rainwater Concentration Data

	Concentration Range (ng/L)	
	Sarnia - rain	Windsor - rain
Acenaphthylene	<50	<50
Acenaphthene	<50	<50
Fluorene	50	<50
Phenanthrene	109 - 683	143
Fluoranthene	84 - 921	322
Pyrene	80 - 692	577

Source:

Sarnia - at Pollution Control Plant, May - October, 1986, wet-preciptation only samples.

Windsor - Little River Poll. Control Plant, August - November, 1985, all blanks less than 50 ng/L; wet precipitation only samples (collector covered during dry weather).

Detection Limit is 50 ng/L. Extractables only.

From: J. Marsalek, pers. comm.

4.3 PAH Uptake in Soils near Industrial Operations

Data on PAH in soils resulting from atmospheric deposition in Ontario are apparently limited to an unpublished study by the MOE on soil concentrations near a Sault Ste. Marie steel mill and at a remote area 75 km to the north, and a study by Daisey et al. (1983) on PAH in soils near a highway in Toronto.

In the Sault Ste. Marie study, soil was collected at two or three depths between the soil surface and 15 cm below the surface. The three sites sampled were within about 750 m of the Algoma Steel mill.

Concentrations of ten PAH ranged from 4 to 9,523 ug/kg in the soil surface, with B[a]A and CHR occurring at the highest levels (Table 4-18). Concentrations generally declined with depth at two of the three sites. In general, PAH concentrations in the soil were one to two orders of magnitude greater near the steel mill than at the control site. The soil concentration in Sault Ste. Marie is generally within the range of PAH concentrations reported for urban soils in the vicinity of Birmingham, U.K. (Table 4-19), although B[a]A and CHR concentrations tend to be somewhat higher and B[a]P concentrations somewhat lower at Sault Ste. Marie.

Daisey et al. (1983) reviewed PAH soil concentrations at a site near highway 401 in Toronto, Ontario. The concentrations of 15 PAH expressed as ratios with respect to B[e]P were reported with fluoranthene and pyrene occurring at the highest levels (Table 4-19). Soil data were also reported for samples collected at sites near a motorway in the Midlands, U.K. The ratios reported were generally higher than those for Toronto.

TABLE 4-18

Concentrations of Polycyclic Aromatic Hydrocarbons in Soil Collected at Different Sites from the Algoma Steel: Sault Ste. Marie Plant July 7, 1980

PAH	Sample Depth (cm)	Concentrations (ug/kg soil) 1 m	14 m	19 m	Control
Fluoranthene	0-5	625	655	235	9
	5-10	446	1000	75	
	10-15	150			
Pyrene	0-5	550	1762	235	13
	5-10	546	560	125	
	10-15	369			
Benz[a]anthracene	0-5	7250	9523	2720	159
	5-10	4658	9250	960	
	10-15	2087			
Chrysene	0-5	6750	9523	2480	168
	5-10	4600	7750	1200	
	10-15	2330			
Benzo[k]fluoranthene	0-5	240	238	68	4
	5-10	134	360	25	
	10-15	57			
Benzo[a]pyrene	0-5	482	310	138	5
	5-10	313	650	54	
	10-15	141			
Dibenz[a,h]anthracene	0-5	40	48	4	ND
	5-10	33	88	4	
	10-15	16			
Benzo[ghi]perylene	0-5	243	429	57	5
	5-10	187	225	44	
	10-15	200			
Anthanthrene	0-5	148	156	30	ND
	5-10	89	320	13	
	10-15	37			

ND = not detectable

From: MOE unpublished data, Air Resources Branch, Phytotoxicity Section.

TABLE 4-19

Ratios of the Concentrations of PAH to Benzo[e]Pyrene in Soil Near Roadways

Compound	PAH/B[e]P Location A	PAH/B[e]P Location B
Anthracene	0.4	ND
Phenanthrene	0.4-1.1	ND
Fluoranthene	1.2-1.8	1.2-3.7
Pyrene	0.9-1.9	0.8-2.5
Benz[a]anthracene	0.8-2.9	0.8-2.0
Chrysene	0.8-2.3	1.1-1.8
Benzo[b]fluoranthene	0.8-1.0	ND
Benzo[k]fluoranthene	0.5-0.6	ND
Benzo[e]pyrene	1.0	1.0
Benzo[a]pyrene	0.9-1.1	0.7-1.4
Perylene	0.3-0.8	ND
Benzo[ghi]perylene	1.2-1.3	ND
Indeno[1,2,3-cd]pyrene	0.7	ND
Coronene	0.1-0.7	0.1-0.3
Anthanthrene	0.2-0.3	ND
ng B[e]P/g soil	95-745	363-2,293

A - Samples collected near Highway 401 in Toronto, Canada.

B - Samples collected near Midlands motorway interchange with heavy traffic in England.

From: Daisey et al., 1983

The Midlands values also correlate well with other Midlands studies carried out in Birmingham, U.K., presented as the last column in Table 4-20. A variety of typical urban sources, principally automotive traffic, was implicated as the major PAH source to soils in Birmingham.

Based on a review by Grimmer (1983), B[a]P levels in soils range widely, from less than 0.02 ug/kg in most areas of Iceland where very little fossil fuel is burned, to 200 mg/kg near an oil refinery in the U.S.S.R. In general, urban soils appear to have 100 to 1,000 ug/kg of B[a]P, with higher concentrations occurring near traffic sources, airports, railroad stations and areas of heavy industry. B[a]P concentrations in Sault Ste. Marie soils appear to be typical of concentrations reported for urban soils from other areas. Background soil concentrations of 5 ug/kg of B[a]P 75 km north of Sault Ste. Marie are probably representative of concentrations in remote areas of Ontario and may reflect fallout from natural sources such as forest fires.

4.4 Municipal Effluents

Zukovs et al. (1984) conducted an extensive evaluation of the Hamilton STP which receives a major industrial waste component. He showed that 95 to 100% of 8 PAH measured in the influent were removed through deposition with sewage sludges. Effluent concentrations averaged 0.04 to 0.8 ug/L (Table 4-21). Total environmental loadings of PAH to Hamilton Harbour were estimated to be 286 kg PAH per year. The PAH profile is presented in Table 4-22 and may be compared with the Ontario MISA data obtained on 37 WPCPs and summarized in Tables 4-7 and 4-8.

TABLE 4-20

Concentrations of PAH in Surface Soil at Different Sites in the Vicinity of Birmingham, U.K.

Compound	PAH Concentration (ug/kg surface soil)								
	Control	1 m	100 m	500 m	600 m	700 m	730 m	940 m	PAH/ B[e]P 1 m
Pyrene	293	4515	1828	1057	1825	300	145	1122	2.0
Fluoranthene	417	3734	1106	1138	2636	275	200	996	1.6
Benz[a]anthracene	290	3297	1868	939	1234	459	169	1065	1.4
Chrysene	566	2703	1686	497	1283	365	251	972	1.2
Benzo[a]pyrene	356	3196	758	442	523	165	170	657	1.4
Benzo[e]pyrene	363	2293	947	461	719	159	164	745	1.0
Coronene	32	322	122	121	151	58	57	70	0.1

From: Butler et al., 1984

TABLE 4-21

Average Concentrations of PAH Discharged from the Hamilton WPCP

Contaminant	Average Concentration (ug/L)	Concentration Range (ug/L)
Acenaphthylene	0.04	0.0-0.54
Fluorene	0.19	0.0-2.05
Fluoranthene	0.61	0.05-3.13
Carbazole	0.41	0.0-1.07
Pyrene	0.80	0.0-4.96
Benzo[a]pyrene	0.62	0.0-2.70

From: Zukovs et al., 1984.

TABLE 4-22

Estimated Output of PAH for Hamilton Waste Treatment Plant*

Contaminant	Out (kg/yr)
Acenaphthylene	4.1
Fluorene	19.0
Fluoranthene	65.7
Carbazole	43.8
Pyrene	84.0
Benzo[a]pyrene	69.4
Total PAH**	286.0

* These estimates are based on average values from 14 sampling days and include very high values measured on one or two days for most contaminants. Thus, these annual averages are considered to be high estimates.

** Estimate based on 6 PAH compounds.

From: Zukovs et al., 1984.

Contamination of aquatic sediments with PAH has been attributed to sewage outfalls. PAH concentrations in sediments were examined at seven stations along a pollution gradient down current from the Los Angeles County Sanitation District's sewage outfalls in California. Data are summarized in Table 4-23.

4.5 Runoff

Surface runoff can contain significant quantities of PAH due to erosion of contaminated soils and contamination by petroleum residues on roadways (Hermann, 1981). Marsalek and Schroeter (1984) measured concentrations of PAH in runoff in 12 urban centres in Ontario to the Great Lakes (Table 4-24). Runoff water levels of each PAH measured 1.0 ug/L or less, while the sediment component contained concentrations of 0.43 to 2.4 ug/g. Mean total PAH loading in the Canadian Great Lakes basin from runoff was estimated at 7.7 tonnes per year (Table 4-25).

Greater loads of PAH (as mass/drainage area/year) have been measured in runoff from highway and industrial land uses in comparison to commercial and residential areas (Hoffman et al., 1984).

PAH measurements made in runoff from four different urban land use areas of Rhode Island were similar in terms of percentage chemical distribution. Fluoranthene and pyrene were most prevalent in runoff while benz[a]anthracene was notably elevated in the industrial runoff area (Hoffman et al., 1984).

TABLE 4-23

Concentration of PAH in Palos Verdes Shelf and Santa Monica Bay Sediments

Compounds	PAH Concentration Range* (ug/kg dry weight)
Acenaphthylene	14-160
Anthracene	35-623
Fluoranthene	92-294
Phenanthrene	290
Benzo[a]anthracene	1330
Benzo[b]fluoranthene	338-633
Pyrene	118-838
Chrysene	606

* Base/neutral compounds.

From: Swartz et al., 1985

TABLE 4-24

Best Estimates of Mean Concentrations of Polyaromatic Hydrocarbons in Urban Runoff

Parameter	Water			Sediment		
	No. of Samples	Freq. %	Mean ppb	No. of Samples	Freq. %	Mean ppm
Quinoline	53	4	1.0	88	17	0.530
Acenaphthylene	53	17	0.96	88	10	0.700
Acenaphthene	53	13	0.97	88	1	0.450
Fluorene	53	2	1.0	88	8	0.490
Phenanthrene	53	6	1.0	88	30	1.700
Fluoranthene	53	13	1.0	87	37	2.400
Pyrene	48	17	1.0	86	28	2.200

From: Marsalek and Schroeter, 1984.

TABLE 4-25

Annual Loadings of Polyaromatic Hydrocarbons in Urban Runoff in the Great Lakes Basin

	Sub-Basin Annual Loadings (kg/yr)					Whole Basin Loading (kg/yr)
Parameter	Erie	Huron	Ontario	St. Clair	Superior	
Quinoline	96	77	385	56	10	624
Acenaphthylene	94	76	378	55	9	612
Acenaphthene	92	75	370	55	9	601
Fluorene	95	77	383	56	10	621
Phenanthrene	108	87	437	63	11	706
Fluoranthene	115	93	467	68	12	755
Pyrene	113	91	459	66	12	741
Total PAH(1)	1179	954	4753	695	119	7700

(1) including contributions for naphthalenes, etc.

From: Marsalek and Schroeter, 1984.

Sixteen PAH in runoff were measured in 28 U.S. cities and 11 PAH were identified at concentrations of 0.3 to 12 ug/L (Cole et al., 1984). Highway runoff and combined sewer overflows were cited as major sources of aquatic PAH by Ellis et al. (1985). Road surface runoff in Norway contained total PAH levels of 1.6 to 11 ug/L and a total of 10 g PAH per km vehicle day was the mean runoff estimate for the whole year (Lygren et al., 1984). Gjessing et al. (1984) showed, however, that PAH in highway runoff were largely retained in adjacent soil surfaces and that a nearby lake was influenced more by atmospheric deposition.

Analysis of nine storm sewer sediment samples along the Niagara River yielded varied concentrations of PAH up to 47 ug/g (Table 4-26). Total runoff of selected PAH to the Niagara River was estimated as 25 kg/yr (Table 4-27).

4.6 Oil Spills

No information has yet been documented concerning PAH loadings to Ontario waters from oil spills. About 0.5 million gallons (2300 m^3) of petroleum products were reported spilled each year in Ontario (P. Belling, Spills Action Centre, MOE, personal communication), excluding occasional larger spills of up to several hundred thousand gallons that occur from time to time. This includes both land-based spills and spills into surface waters. Data on quantities of each type of petroleum product are not available. In addition, the content is dependent on the petroleum product and therefore will vary considerably. An example of the PAH profile in used motor oil is presented in Table 4-28.

TABLE 4-26

New York Storm Sewer Sediment Analysis of PAH (Niagara River, Dry Conditions)

	Number of Times Identified	Number of Samples	Maximum Concentration (ug/g)
Ace	6	9	ND
A	8	9	47
B[a]A	5	9	2.4
B[a]P	4	9	2.5
B[b]F	5	9	ND
B[ghi]Per	1	9	ND
B[k]F	0	9	-
Chr	7	9	3.5
DB[ah]A	1	9	ND
F	4	9	24
Fln	6	9	28
I[1,2,3-cd]P	2	9	ND
Phen	7	9	ND
P	8	9	22

ND - no data

From: IJC, 1987a.

TABLE 4-27

Total Loadings of PAH to Niagara River in Runoff (Water Plus Sediment)

PAH	Best Estimate (kg/yr)
Acey	0.74
Ace	0.88
Fln	0.67
Phen	3.2
F	4.3
P	15
Total	24.8

From: Niagara River Toxics Committee, 1984.

TABLE 4-28

Polycyclic Aromatic Hydrocarbons in Used Motor Oil

PAH	Concentration (mg/L Oil)
Fluorene	1.5
Phenanthrene	7.8
Anthracene	0.3
Methylphenanthrenes	9.2
Fluoranthene	4.4
Pyrene	6.7
Benzofluorenes	2.8
Benzo[c]phenanthrenes	0.1
Benz[a]anthracene	1.1
Chrysene & triphenylene	2.5
Benzo[k]fluoranthene	1.4
Benzo[e]pyrene	1.7
Benzo[a]pyrene	0.4
Perylene	0.1
Benzo[ghi]perylene	1.7
Total PAH*	82.5

* The total includes other alkyl-substituted PAH as well as PAH not included in the priority list for this document.

From: NRC, 1983.

4.6.1 Refinery Losses to Water

Losses from refineries as effluent to the aquatic environment may also occur. An estimate of such losses in Ontario is presented in Table 4-29. The total aquatic loading of PAH is estimated to be 80 kg/yr for all Ontario from refineries (PACE, 1987).

4.6.2 Gasoline and Diesel Oil Loss During Tank Refilling

All gasoline and diesel fuel oils contain PAH compounds. For example, a commercial diesel fuel has been found to contain the following: phenanthrene (202 mg/L); anthracene (1.9 mg/L); pyrene (50.2 mg/L); B[b]F (13.8 mg/L); and B[a]P (1.9 mg/L) (Obuchi et al., 1984).

No data are available for gasoline or diesel oil loss during refilling of vehicles. If approximately 0.5 mL were lost and the average tank capacity is 40 L, then a conservative estimate of the annual loss would be 0.0005/40 of the total yearly gasoline utilization, that is, $1.25 \times 10^{-5} \times 8{,}526{,}390 = 106.6$ kL/yr. For a total PAH content of 270 mg/L and a B[a]P content of 1.9 mg/L this corresponds to a discharge to soil in Ontario of 28.7 kg PAH/yr and 0.2 kg B[a]P/yr.

4.6.3 Waste Oil from Transportation

Although no data on oil spills from mobile sources are available for Ontario, a rough estimate can be made based on the ad-hoc assumption that about 1 L of oil is spilled per year by each fit and active vehicle operating in Ontario. From this assumption, it can be inferred that for a fleet of 5,807,720 vehicles including automobiles, light trucks and two stroke engines, that approximately 5,800 kL are lost annually to the soil.

TABLE 4-29

Estimated PAH Losses from Ontario Refineries in Wastewater[1]

PAH	Total Load[2] (kg/yr)
Acenaphthene	0.0
Acenaphthylene	0.0
Anthracene	0.85
Benzo[a]anthracene	2.4
Benzo[k]fluoranthene	0.42
Benzo[a]pyrene	0.0
Fluoranthene	0.0
Fluorene	14
Phenanthrene	31
Pyrene	8.9
Chrysene	21
Total PAH	78.6

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[1] From total crude oil transformed to refined products of 26,685,100,000 L or 133,425,500 barrels in 1986.

[2] Concentration, flow and BPSD (barrels per stream day) data from PACE Report No. 80-4.

Assuming an average PAH concentration of 82.5mg/L and a B[a]P concentration of 1 mg/L, it is estimated that 478 kg PAH and 5.8 kg B[a]P are spilled annually.

4.6.4 Disposal of Dredging Spoils

It is likely that the deposition of dredging spoils in the aquatic environment results in no net PAH loading change for the province, but involves instead the transport of PAH from one location to another. Because harbours and river mouths tend to be areas of contaminant deposition and areas where considerable dredging is required, the quantities of PAH in dredged sediments in Ontario waterways may be substantial.

4.7 Leachate from Waste Disposal Sites

Leachate contamination from localized PAH sources has been identified. A simulation of rainfall runoff from model coal piles, for example, demonstrated that many PAH can be released, although most estimated individual PAH concentrations were less than 50 ug/L (Stahl, 1984). Extreme case simulations resulted in individual PAH levels that were less than 1 ug/L (limit of detection) to 107 ug/L (Table 4-30).

4.8 Treated Wood Structures for Piers

The use of preserved wood in piers and other harbour structures has been shown to result in PAH contamination of the aquatic environment. Lake et al. (1979) reported elevated sediment PAH concentrations near piers treated with coal tar.

TABLE 4-30

Organic Compounds Identified in Extracts of Runoffs from Different Coals

Compound	Estimated Concentration (ug/L) Illinois #6 Coal	 Kentucky Coal
Acenaphthene	1	-
Fluorene	5	-
Phenanthrene	65	195
Anthracene	0.6	-
Fluoranthene	3	67
Pyrene	4	-
Chrysene	1	25
Benz[a]anthracene	2	29
Benzo[k]fluoranthene	0.6	-
Benzo[a]pyrene	0.6	30

Concentration refers to that in the original runoff.

- no data

From: Stahl (1984).

In Atlantic Canada, Eaton and Zitko (1978) found 25.7, 35 and 48 ug/g F, P and B[a]A, respectively in sediments near a creosoted wharf. No information was found on PAH contamination of surface waters from railway ties or utility poles, although it is probable that some PAH losses to surface water environments also occur from these widely used items.

Total runoff/leachate volume estimates have been made for coal pile sites at the four operating coal-fired generating stations in Ontario (Table 4-31). Based on the concentration data presented by Stahl et al. (1984), the total yearly PAH losses from coal piles at Ontario generating stations, are estimated to be in the range of 3.8-46.9 kg/yr (Table 4-32).

Coal and oil gas manufacturing plants operated in 36 Ontario communities from the mid 1880s until the mid 1950s provide gas for a local domestic and industrial consumption. Intera Technologies Ltd. (1987) conducted a reconnaissance of manufactured gas plant locations to evaluate the potential for adverse environmental effects from buried wastes from these plants.

Wastes from these plants include tars, sludges, liquors and other gas cleaning wastes that are rich in PAH. Many sites were qualitatively assessed as currently impacting off-site properties and water resources, indicating that these probably represent significant PAH sources to local surface water environments. Unpublished MOE data on PAH concentrations in sediments and water downstream from a coal gas waste site at Port Stanley confirm this assessment (D. Veal, OME, pers. comm.).

TABLE 4-31

Estimated Yearly Volumes of Coal Pile Runoff and Leachate at Coal-Fired Generated Stations in Ontario

Station[1]	Coal Pile Area (ha)[2]	Precipitation Minus Evapotranspiration (mm/year)	Total Runoff/ Leachate (m^3/yr)
1	13	200	26,000
2	19	200	38,000
3	28	200	56,000
4	6.4	200	12,800

[1] Station identification confidential.

[2] From Dearborn (1982).

[3] Estimated from precipitation and evapotranspiration rates provided by Fisheries and Environment Canada (1978).

TABLE 4-32

Estimated PAH Loadings from Ontario Generation Stations Coal Pile Runoff

PAH	Estimated Concentration in Runoff (ug/L)	Annual PAH Loading* (kg/yr)
Acenapthene	1	0.13
Fluorene	5	0.66
Phenanthrene	11-195	1.5-25.9
Anthracene	0.6	0.08
Fluoranthene	3-67	0.4-8.9
Pyrene	4	0.5
Chrysene	1-25	0.1-3.3
Benz[a]anthracene	2-29	0.3-3.8
Benzo[k]fluoranthene	0.6	0.08
Benzo[a]pyrene	0.6-30	0.08-4.0
Total PAH**		3.8-46.9

* Based on a total runoff from 4 coal-fired generating stations of 132,800 kL/yr.

** Based on 10 PAH.

From: Stahl (1984).

4.9 Transboundary Movement of Polycyclic Aromatic Hydrocarbons

PAH are not as mobile in the aquatic environment as in the atmosphere. Rapid sorption and sedimentation prevent long range transport, resulting in elevated concentrations near their source (Eisler, 1987). The transport distance would be a function of physical processes, such as particle size, currents and size of the water body, as well as physio-chemical and biological degradation processes.

PAH occurring in the water column, either in suspended particulate or dissolved form, may be transported downcurrent. Because PAH usually occur in low concentrations in surface waters, and because analytical techniques for quantification of PAH at low concentrations have been of questionable reliability, relatively little information exists on surface water transport of PAH.

Environment Canada has an ongoing project to monitor water quality entering (Fort Erie) and leaving (Niagara-on-the-Lake) the Niagara River, in order to discern the contributions of toxic substances entering the river from Lake Erie and from sources along the river. The difference in PAH flux between the source and mouth of the river represents the PAH loadings from all sources (industrial, hazardous waste site seepage, runoff, etc.) along the course of the river. Data are available for 11 PAH, based on analysis of suspended sediment (concentrations were less than detection limits in the dissolved phase). Table 4-33 shows PAH mean loading estimates for these compounds from inputs from Lake Erie to the river, outputs from the river to Lake Ontario, as well as sources along the river (IJC, 1987a). Urban runoff data for the Niagara River (Table 4-34) indicate that this source (25.5 kg PAH/yr) represents a small fraction of the total loadings along the course of the river (14.5 MT/yr).

TABLE 4-33

Loadings of PAH to the Niagara River

	Loadings (kg/day)		
	Fort Erie	Niagara on-the-Lake	Niagara River Loading (by difference)
Acenaphthene	0.05	0.43	0.38
Anthracene	0.40	1.25	0.85
Benzanthracene	1.50	8.05	6.55
Benzo[a]pyrene	1.23	3.78	2.55
Benz[a,h]anthracene	0.57	2.18	0.61
Benzo[b&k]fluoranthene	1.66	9.72	8.06
Chrysene	0.81	4.60	3.79
Fluorene	3.85	11.44	7.59
Fluoranthene	0.13	0.54	0.41
Phenanthrene	2.58	6.07	3.49
Pyrene	3.07	8.58	5.51
Total PAH	15.8	55.6	39.8

Based on analysis of suspended sediment samples from water samples, December 1984 to March 1986.

From: IJC, 1987a.

TABLE 4-34

Annual Total Loadings of PAH in Water and Sediment in Urban Runoff for the Niagara River

PAH	Estimated Loading (kg/yr)
Quinoline	0.74
Acenaphthylene	0.74
Acenaphthene	0.88
Fluorene	0.67
Phenanthrene	3.2
Fluoranthene	4.3
Pyrene	15.0
Total PAH	25.5

From: IJC, 1987a.

Bahnick and Markee (1985) monitored PAH concentrations on suspended sediment in the St. Louis River at Duluth, and estimated annual loadings from the river to Lake Superior (Table 4-35). The authors noted that these local loadings to the lake are very small relative to atmospheric deposition estimated for Lake Superior by Eisenreich et al., (1981).

Comba et al. (1985) presented detailed data on PAH partitioning in surface water (particulate and total), surficial sediment, sediment pore water and in the water surface microlayer in the Detroit River. This information provides considerable information on partitioning and transport processes for PAH in the Detroit River. Data collected by the National Water Research Institute on PAH in the St. Clair River are presented in Table 4-36 and illustrate the emission profile of 24 industrial point source discharges (Environment Canada/MOE, 1987); however, no flow rate data were available to estimate loadings to the river.

4.10 Summary of PAH Emissions to Soil and Water

The annual PAH emission rates in the form of precipitation and as municipal or industrial liquid discharges as well as in the form of sludge application to the Ontario ecosystem are presented in Table 4-37. They indicate that the single largest contributor of PAH to soil and water is through atmospheric preciptation.

TABLE 4-35

Input of Particulate-Associated Contaminants to Western Lake Superior from the St. Louis River and Duluth Harbor Area

Parameter	Particulate Concentration (ug/g)	Particulate Transport Lake Superior* (kg/yr)
Fluorene	0.15	0.42
Phenanthrene	1.04	2.9
Methylanthracene	0.06	0.17
Fluoranthene	1.88	5.3
Pyrene	1.76	4.9

* Based on a discharge rate of 30 m^3/sec, an average suspended solid concentration of 10 mg/L and 30% particulates input to the lake.

From: Bahnick & Markee, 1985.

TABLE 4-36

PAH Emission Profile from 24 Point Source Discharges to the St. Clair River

PAH	Concentration (ug/L)
Acenaphthylene	4.14
Acenaphthene	1.17
Fluorene	2.80
Phenanthrene	3.39
Anthracene	0.76
Fluoranthene	0.94
Pyrene	1.26
Benz[a]anthracene	0.34
Chrysene	0.71
Benzo[b]fluoranthene	0.30
Benzo[k]fluoranthene	0.06
Benzo[a]pyrene	0.79
Indenopyrene	0.86
Dibenz[ah]anthracene	0.76
Benzo[ghi]perylene	0.94
Total PAH	19.2

From: Environment Canada/MOE, 1987.

TABLE 4-37

Estimated PAH Loadings to the Soil and Water

Source and Input	PAH Loadings (MT/yr)	%	Global PAH Loading* %
Atmospheric			
Precipitation	109	75	17-42.5
Soil			
Land treatment (sewage sludge)	0.3-1.3 (as B[a]P)	3.7**	0.8-2.0
Crankcase Oil	0.5	0.3	
Gasoline Spills	0.03	0.03	
Water			51.6-80.4
Water Pollution Control Plants (WPCP)	7.2	5.0	
Hamilton WPCP	0.3	0.2	
Leachate (coal piles)	0.004 - 0.05	0.02	
Runoff (to Great Lakes)	7.7	5.3	
Urban Runoff to Niagara River	14.5	10	
Petroleum Refineries	0.08	0.6	
Biosynthhesis	neglig.	0	1.3-3.4

neglig. - negligibly small

* From: NRCC, 1983. (The estimate in this citation is based on a significant contribution from marine petroleum spillage which does not apply to Ontario.)

** Estimated by assuming a PAH : B[a]P ratio of 6.7:1

5.0 ENVIRONMENTAL PROCESSES AND FATE OF PAH

5.1 Introduction (Air)

The literature on the fate of polycyclic aromatic hydrocarbons (PAH) in the environment is limited. The pathways open to these compounds are expected to be no different from those available to other predominantly particulate species in the same size range. The principal reaction proucts of atmospheric processes which are of interest are the oxy- and nitro-PAH.

There have been no reports on studies to determine the particle size distribution of ambient oxy- and nitro-PAH, but several studies have established that the parent PAH compounds are predominantly in the size fraction less than 1 um aerodynamic diameter (Pierce and Katz, 1976; Demaio and Corn, 1966; Butler and Crossley, 1981). Currently, all indications are that PAH and their oxy- and nitro-PAH compounds would be expected to have similar size distributions.

The particulate oxy-and nitro-PAH may undergo dispersion over hundreds of kilometres in the process of long range transport (LRT), deposition and chemical transformation. The LRT of oxy- and nitro-PAH is expected to be similar to that of the parent of PAH and such transport is expected to account for the presence of these compounds in remote areas.

Deposition of oxy- and nitro-PAH compounds is also expected to be similar to that of PAH. The dry deposition processes should be described by those of 1.0 um particles which have deposition velocities, V_d, of the order of 0.02 to 0.32 cm/s based on estimates by Sehmel (1980) or Cawse (1974), as noted by Strand and Andren (1980). Similerly, during wet deposition, scavenging ratios for oxy- and nitro-PAH should be no different from those of particles of 1.0 um or less. Because of somewhat enhanced solubility, the highly oxidized oxy-derivatives (acids and anhydrides) may prove to have higher washout ratios. Information on the presence of these oxy-PAH derivatives in ground water may provide useful information on the deposition processes to water bodies.

5.1.1 Chemical Reactivity (Atmospheric Aspects)

PAH exist in the atmosphere in the vapour phase or bound to particles. Their chemical reactivity in the atmosphere is determined not only by the inherent molecular structure of the PAH but also by the physical and chemical nature of the substrate on which PAH are adsorbed, on the concentrations and composition of gases and on the intensity of absorbed radiation. Chemical reactivity of PAH has been investigated theoretically and experimentally. The former investigations have been based on structure-reactivity relationships that have been derived from molecular orbital calculations or empirical correlations with various types of reactions.

The atmospheric reactivity of particle-bound PAH is limited by the lifetime of the particle in the atmosphere. Particles are removed from the atmosphere by diffusion, sedimentation and wet scavenging processes. Superimposed on these processes are the photochemical and thermochemical reactions with atmospheric species which transform PAH and contribute to the determination of their atmospheric lifetimes. The transformation reactions of PAH, which include nitration reactions, reactions with oxygen species (ozone, oxygen atoms and excited state molecular oxygen species), and sulphur oxides, as well as photolysis reactions, are described in this section. Rate data are summarized (expressed as half lives or as relative rates) for these transformations. The determination of the rates of PAH transformation has relied on experimental conditions which have not always adequately simulated natural conditions; hence reported rates may be more appropriately viewed in terms of the relative rates for a series of PAH. Selected studies in which reaction rates are available for relevant reactions that pertain to the atmospheric reactions, as well as the occurrence and fate of PAH products are presented in Table 5-1. The following sections focus on those investigations which are most representative of natural atmospheric conditions based on the half lives for relevant reactions.

5.1.1.1 Particle Lifetime

Since most of the PAH of interest occur adsorbed to particles in the atmosphere, the lifetimes of particles represent an upper limit for the atmospheric lifetime of particle-bound PAH. Particle lifetime is very dependent on the aerodynamic diameter.

Particles in the 1-10 um diameter range have been estimated to have lifetimes of 100-1000 h (Esmen and Corn, 1971). These estimates assumed a mixing height of 2 km, a monotonic non-increasing flux and a monotonic non-increasing concentration-height function. The lifetime estimates approximate to the dry deposition process. Consideration of the wet deposition process was included in estimating the physical residence time of PAH by Mueller (1984). Laboratory measurements were used to estimate chemical lifetimes for pyrene (18 h), B[e]P (96 h) and B[ghi]P (96 h). The overall mean lifetimes (expressed as the inverse of the sum of the reciprocal physical and chemical lifetimes) were 16 h, 48 h and 6 h for pyrene, B[e]P and B[ghi]P, respectively.

TABLE 5-1

Summary of Photolytic and Electrophilic Reactions of PAH and Nitro-PAH

Activator	PAH/Substrate	Products/Comments
Light	PAH solutions evaporated on thin layer petri dishes. A (0.2), B[a]A (4.2), DB[a]A (9.6), DB[a,c]A (9.2), P (4.2), B[a]P (5.3), B[e]P (21.1), B[b]F (8.7), B[k]F (74.1).	Half lives in hours in brackets. Lane and Katz, 1977.
Light	Tropospheric lifetimes A < B[a]F < B[a]A < B[j]F < B[b]Chr < B[a]P < B[k]F < B[b]F < F < < P measured by photooxidation on silica gel substrate.	Photooxidation rates similar to Lane et al., 1977. Blau and Gustan, 1982.
Light	Effect of heating to 400°C presampled and clean Hi-Vol filters. Extract with cyclohexane. Half lives estimated for PAH in collected particulate. P (11.9 h), B[a] (14.4 h), B[a]P (11.6 h).	P and B[a]P stable on glass fibre filters. Heat enhanced photodegradation. Cyclohexane solvent increased photodegradation of P. Valerio et al., 1984.
Light	Photolysis of P and B[a]P on coal ash, alumina, silica gel and flaked graphite.	No quantitative data. Thermal decomposition of B[a]P and P on substrates negligible. Yokley et al., 1986.
Light	Fifteen PAH adsorbed on silica gel, alumina, flyash and carbon black. Half lives with flyash as adsorbent ranged from 29-49 hours.	Behymer and Hites, 1985.

TABLE 5-1 (cont'd)

Summary of Photolytic and Electrophilic Reactions of PAH and Nitro-PAH

Activator	PAH/Substrate	Products/Comments
Light	Woodsmoke and sunlight in a Teflon chamber. With/without <30 ppb NO_2 and/or <10 ppb O_3. Half lives (mins): B[a]A (54 min.), CHR + TRI (196), B[b]F (232), B[k]F, B[j]F, B[k]F and B[j]F (156), B[a]P (69), B[ghi]Per (100).	Photodegradation slower at -7°C than 20°C. Kamens et al., 1986.
HNO_2, NO_2, HNO_3, O_3 (0.2 ppb)	No degradation of PAH with 0.1-1.0 ppm HNO_2 during sampling. 10-nitro B[a]A, 6-nitro B[a]P, 3-nitro P found for 0.12 ppm NO_2 reaction with PAH.	Lindskog, 1983.
	HNO_3 leads to significant degradation of B[a]A, B[a]P, Per and B(ghi)Per from 20% to 55%.	
N_2O_5	Pyrene, perylene adsorbed on glass fibre filters. Pyrene 0.3% (12 h) nitrated product per hour $[N_2O_5]$ = 0.6 ppb.	No reaction with NO_3. Relative reaction rates with N_2O_5 different from that with HNO_3 in solution. Per < P for N_2O_5 - converse for HNO_3 in solution.
	Upper limit of 1.8%/h for $[N_2O_5]$ = 14 ppb.	Pitts et al. (1985b).

5.1.1.2 Reactions with Nitrating Species

The nitration reactions of PAH have commanded much attention in view of the mutagenic (Rosenkranz and Mermelstein, 1983) and carcinogenic (Hirose et al., 1984; Ohgaki et al., 1984, 1985; Tokiwa and Ohnishi, 1986) properties of their nitro-PAH reaction products. The nature and origin of the nitro-PAH are important in order to assess the potential health impacts of PAH and nitro-PAH. The nitration reactions have been investigated using deposits of pure PAH on filters, PAH adsorbed on various solid particle substrates and in reaction chambers.

The reactions of pure PAH (deposited on filters) with nitrating species have been studied by several investigators (Pitts et al., 1980b; Tanner and Fajer, 1983; Tokiwa et al., 1981; Grosjean et al., 1983a). B[a]P deposited on clean glass fibre filters was transformed to the 1-, 3-, and 6-nitroB[a]P by NO_2 with traces of HNO_3 (Pitts et al., 1978b; Pitts, 1979) or by HNO_3 only (Grosjean et al., 1983b). Similarly, exposures of perylene to NO_2 and NO_2/HNO_3 mixtures yielded nitration products with significant yields only when nitric acid was present. Earlier studies (Pitts et al., 1978b; Jager and Hanus, 1980; Hughes et al., 1980; Butler and Crossley, 1981; Tokiwa et al., 1981; Brorstroem et al., 1983a; Lindskog, 1983) reported reactions of PAH (present in ambient or diesel exhaust particulates) with NO_2, but the losses of PAH should properly have been ascribed to reaction to traces of HNO_3 (Grosjean et al., 1983a).

The nitration by N_2O_4, HNO_2 and HNO_3 of 25 PAH in solution was studied to investigate the reactivity of PAH to nitrating species that are relevant in atmospheric chemistry (Nielsen, 1984). A classification of various PAH in which the Class I compounds are most reactive and Class VI least reactive, was established (Table 5-2). The classification was based on the relative rate constants for electrophilic nitration reactions in solution (Nielsen, 1984; Dewar et al., 1956) as well as on observed correlations between rates of nitration reactions and spectroscopic properties (the position of the first p-band), the aromaticity index or the first ionization potential.

The classification is consistent with several features of the occurrence of PAH and nitro-PAH in environmental samples. For example, the PAH compounds in Class I, the most reactive, have not been identified in environmental samples. Similarly, the compounds in Class II have been shown to react with NO_2 and HNO_3 under a variety of conditions, whereas less reactive compounds, e.g., coronene, in Class IV were more resistant to attack by NO_2. The classification, although preliminary, offers a reasonable basis for anticipating the occurrence of some nitro-PAH in environmental samples. However, the authors pointed out that the relative reactivity of PAH implied by the classification may be altered when photo-activation is involved.

The nature of the substrate (on which PAH are absorbed) alters the reactivity of the PAH substantially (Korfmacher et al., 1980a). For example, a different product distribution is found in photoactivated nitration (Pitts et al., 1983), when compared to nitration in solution, thus a different mechanism for such reactions is implied. In contrast, the relative rates of disappearance of several PAH on (dark) reaction with NO_2 (Nielsen et al., 1983a; Tanner and Fajer, 1983) were consistent with Nielsen's classification scheme. Wehry et al. (1984) made similar conclusions based on reactions of NO_2/HNO_3 mixtures and NO_2 separately with PAH adsorbed on coal fly ashes, alumina, silica or graphite.

TABLE 5-2

Classification of PAH Based on Electrophilic Nitration Reactions

Class I

dibenzo[a,h]pyrene

Class II

anthracene
benzo[a]pyrene
dibenzo[a,l]pyrene
dibenzo[a,i]pyrene
perylene

Class III

benz[a]anthracene
benzo[g]chrysene
benzo[ghi]perylene
dibenzo[a,e]pyrene
pyrene

Class IV

benzo[c]chrysene
benzo[c]phenanthrene
benzo[e]pyrene
chrysene
coronene
dibenzanthracenes
dibenzo[e,l]pyrene

Class V

acenaphthylene
benzofluoranthenes
fluoranthene
indeno[1,2,3-cd]pyrene
phenanthrene
triphenylene

From Nielsen, 1984.

Since particle-bound PAH present a complex heterogeneous physical and chemical reaction system, several investigators have examined nitration reactions of PAH adsorbed on various 'model' substrates. While some of the laboratory investigations of PAH nitrations on various substrates have yielded relative rate information that is consistent with the nitration rates in solution, the rates and mechanisms of the particle-bound PAH nitration reactions are different from the solution phase nitrations. The complexity of the particle-bound nitrations make estimation of their influence on the lifetime of particle bound PAH difficult.

Recent investigations have relied on chamber studies and in the isolation and speciation of the nitroarene product distribution in order to determine the rates and mechanisms of nitration reactions, especially in polluted atmospheres. The relative rates of reaction of six PAH towards N_2O_5 was found to decrease in the order pyrene > fluoranthene > B[a]P > benz[a]anthracene > perylene > chrysene, in contrast to the order expected on the basis of the nitration reactions in solution. The mechanism of nitration by N_2O_5 is therefore different from that in solution (Pitts et al., 1985a). The nitration of PAH by N_2O_5 is important in view of the presence of N_2O_5 in the atmosphere and, therefore, its role in influencing the atmospheric lifetime of PAH. A nitration rate for pyrene by N_2O_5 at night was estimated at 1.8% h^{-1} (Pitts et al., 1985b).

More recent studies recognize (Pitts et al., 1986; Atkinson et al., 1986; Pitts et al., 1985b) the importance of N_2O_5 and NO_3 as well as the role of OH radicals. The nitration of perylene and pyrene by N_2O_5 rather than by NO_3 was demonstrated by Pitts et al. (1986) and earlier studies implicating nitration by HNO_3 exclusively (Grosjean, 1983) were shown to be due to N_2O_5 (Pitts et al., 1986).

Nitro-PAH found in ambient air include 1- and 2-nitronaphthalene, 1-nitropyrene, 2-nitropyrene, 2-nitrofluoranthene, 3-nitrobiphenyl and 4-nitrobiphenyl. The two most abundant particulate nitro-PAH in ambient samples are 2-nitrofluoranthene and 2-nitropyrene, and their presence has been ascribed to atmospheric nitration reactions (Arey et al., 1987) rather than to direct emissions from combustion sources (Tokiwa and Ohnishi, 1986). The nitro-PAH isomers found in the atmosphere are consistent with the their formation through reactions of parent PAH with OH radicals in the presence of NO_x (Atkinson et al., 1987; Arey et al., 1987). The most abundant nitro-PAH found in ambient samples have been shown to be the more volatile, vapour-phase nitro-PAH such as 2-nitronaphthalene and 3-nitrobiphenyl (Arey et al., 1987). These isomers are not those expected from electrophilic nitration reactions of the parent PAH, but rather, as a result of the atmospheric transformation by atmospheric nitrating species (OH in the presence of NO_x and N_2O_5). Measurements of nitro-PaH at industrial and remote sites showed that 1-nitropyrene concentrations were higher at the most remote site (Bermuda) than at sites near industrial sources in Michigan (Gibson, 1986). The ratio of B[a]P to TSP at sites near the sources were considerably higher than B[a]P/TSP ratios at the distant sources which indicates the importance of the transformation reactions of B[a]P during transport. The formation of 1-nitropyrene during transport was suggested.

The more volatile PAH are abundant in the atmosphere and their lifetimes with respect to OH and nitration reactions are expected to be of the order of 9 h for phenanthrene and 2 h for anthracene (Bierman et al., 1985; Atkinson, 1986). The formation of nitro-PAH by two pathways, one involving OH radicals in the presence of NO_x, and the other due to reaction with N_2O_5, have been shown to be important for 2-nitrofluoranthene and 2-nitropyrene (Arey et al., 1986). Estimates of the half lives of fluoranthene with respect to the OH/NO_x and the N_2O_5 reactions (under southern California conditions) were approximately 6 h and 7 weeks respectively. In Ontario urban atmospheres, NO, NO_x and O_3 concentrations of 400, >500 and 90 ppb respectively have been observed - similar to those in Southern California and ambient concentrations of naphthalene (vs 2800 ng/m^3), fluoranthene (vs 9.7 ng/m^3) and pyrene (vs 12 ng/m^3) for example are similar (see Arey et al., 1987). Thus the nitroarene concentrations and the half lives of the parent PAH with respect to these reactions in Ontario air could be similar to those determined for more southerly latitudes, under certain conditions.

The fate of the nitroarenes - especially those formed in atmospheric nitration reactions, needs to be considered in the overall assessment of PAH. The limited information on the photochemistry of the nitroarenes indicates that quinone products are formed. The photolysis of 9,10-nitroanthracene (absorbed on silica gel) forms the 9,10-anthraquinone, while 6-nitroB[a]P forms the 1,6-, 3,6-, and 6,12- isomers of B[a]P quinones. Analogous photoxidation products are expected for other nitroarenes. Finlayson-Pitts and Pitts (1986) proposed a schema to predict the relative photolysis rates for nitroarenes, and the relatively rapid photolyses of the 6-nitroB[a]P and 1-nitropyrene - both of which are present in polluted atmospheres, are consistent with the predictions. Further work is needed to establish the fate of nitroarenes - especially those formed in atmospheric nitration reactions.

5.1.1.3 Reactions with Ozone

The solution phase reactions of B[a]P with ozone provide a simple model system on which some of the reactions of ozone with PAH may be based. Ozonolysis of B[a]P in solution (methylene chloride, 3:1 methylene chloride-methanol) forms the 3,6- and 1,6-diones of B[a]P. With excess ozone, more highly oxidized products 7H-benz[d,e]anthracen-7-one 3,4-dicarboxylic and 1,2-anthraquinone dicarboxylic acid are formed (Moriconi et al., 1961). Confirmation of the mechanism was not feasible but one of three schemes involving a two-step electrophilic attack by ozone at the most reactive centres (i.e., carbons with the lowest carbon localization energies) to give a sigma complex followed by nucleophilic 1-4 addition to give a primary ozonide and thence to p-quinones was thought to be applicable.

Several investigators have exposed PAH (from previously collected ambient or source particulates or pure compounds deposited on filters or evaporated onto glass surfaces) to ozone (Lane and Katz, 1977; Pitts, 1979; Pitts et al., 1980a; Peters and Siefert, 1980: Rajagapolan et al., 1983; Brorstroem et al., 1983a; Grosjean et al., 1983b; Lindskog et al., 1983). Most studies reported the disappearance of the reagent PAH, but few identified reaction products. B[a]P quinones (1,6-, 3,6- and 6,-12 isomers) were identified by Rajagapolan et al. (1983), B[a]P dihydrols, B[a]P diphenols and B[a]P-phenol and B[a]P-quinones (van Cauwenberghe et al., 1979; Pitts, 1979) and ring-opened compounds including dialdehydes, dicarboxylic acids, ketocarboxylic acids and benzo[a]pyrene-4,5 oxide (Pitts et al., 1980a) were also identified. In contrast, Grosjean et al. (1983b) found no evidence of reaction, but the exposure conditions used (3 hours, 100 ppb ozone) were milder than those in previous studies.

The relative rates of disappearance of several PAH in diesel particulates exposed to ozone were found to be consistent with electron density calculations (van Vaeck and van Cauwenberghe, 1984). No products were identified and the data were consistent with earlier work by Lane and Katz (1977). The presence of several oxy-PAH in ambient samples suggests the oxidation of PAH by ozone could be important in determining the nature of compounds found in ambient samples.

The most relevant investigations of the atmospheric stability of PAH have been derived from outdoor reaction chamber studies in which PAH from woodsmoke were reacted with ozone and nitrogen oxides under natural daytime solar radiation and in the dark (Table 5-3). The half lives of PAH on woodsmoke particles exposed to ozone (540 ppb), to NO_2 in the dark and to 300 ppb O_3, ranged from 30 to 60 minutes. The reaction of B[a]A was found to be very temperature dependent - the half life decreasing by a factor of four to ten for temperatures decreasing from 20 to -7°C (Kamens et al., 1986). PAH decay at lower temperatures and solar intensities, such as would apply in Ontario, therefore, would extend the half lives to several hours. The more complete characterization of the ozone reactions with a wider range of PAH is needed.

5.1.1.4 Reactions with Sulphur Oxides

The reactions of PAH with sulphur oxides have been investigated by Jager and Rakovic (1974), Hughes et al. (1980), Butler and Crossley (1981), Tebbens et al. (1966) and Grosjean et al. (1983a).

PAH absorbed on fly ash or alumina reacted with SO_2 to form several sulphur-containing compounds including pyrene-1-sulphonic acid, pyrene-disulphonic acid, B[a]P-sulphonic acid (Jager and Rakovic, 1974).

TABLE 5-3

Outdoor Chamber Studies of PAH Reactions with O_3, NO_2 and hv[1]

PAH		Half Life (minutes)	
	hv[2]	200 ppb O_3[3]	500 ppb NO_2[3]
Pyrene	42.5	271	
B[a]A	45	186	224
Chr/Tri[4]	61.9	335	224
B[b]F	84.5		
B[k]F	48.8	173	227
B[a]P	37.1	235	224
B[e]P	106		

[1] Kamens et al., 1985
[2] Average total solar radiation intensity 1.2 cal cm^{-2} min^{-1}
[3] Reaction in the dark. Ozone half lives estimated based on rate constants derived at 570 ppb O_3.
[4] Chrysene/triphenylene

In contrast, Hughes et al. (1980) using PAH adsorbed on coal fly ash, alumina, silica and activated charcoal, found no reaction due to SO_2, but SO_3 produced unidentified products. Similar studies by Butler and Crossley (1981), but with PAH on soot, showed no effect due to SO_2, but Tebbens et al. (1966) did report degradation of B[a]P (products not identified) by SO_2.

The solution phase reaction of anthracene with SO_2 is photocatalyzed yielding anthracene-9-sulphonic acid (Nagai et al., 1986). Pyrene also reacts with concentrated H_2SO_4 to give a mixture of sulphonic acids (Valkman et al., 1937). These reactions suggest that it is theoretically possible for PAH to react with SO_2 or H_2SO_4 in the environment to form sulphonic acids. These water soluble compounds have not been identified in ambient samples but this may be due to the use of inappropriate solvents for the extraction of ambient particulates (Nielsen et al., 1983b). If any sulphonic acids formed react further to form sulphonates, extraction methods used in the above studies to isolate sulphonic acids would miss the sulphonates.

5.1.1.5 Photolysis of PAH Compounds

The photochemistry of PAH has been studied for many years. The low temperature solid state photochemistry of condensed hydrocarbons has provided a wealth of information on the spectroscopic properties of molecules and the photophysical processes subsequent to absorption of photons. Of importance to the photochemistry of PAH in the environment is information on the accessibility and stability of excited photochemical states. PAH in environmental matrices are adsorbed to the fine particulate matter and effects of the sorbent on the photochemical properties of PAH are likely to be important.

The solid state photolysis of the pure PAH as well as their solution phase photochemistry are limited, but the photochemistry of PAH adsorbed on various real-environment and model sorbents has been studied by several investigators.

The photolysis of pure PAH (B[a]P, benzo[b]fluoranthene and benzo[k]fluoranthene) deposited on petri dishes was reported by Lane and Katz (1977). They pointed out that surface reactions (photolysis and reaction with ozone, for example) are likely to be important. The effect of the nature of the particles onto which PAH are absorbed is therefore likely to affect the photoreactivity. The spectral distribution and intensity of the light source used were similar to sunlight, but the PAH substrate (solutions of PAH evaporated in petri dishes) was not the same as present in natural conditions.

Sorbents used have been soot (Thomas et al., 1968; Tebbens et al., 1971), particles on glass fibre filters (Fox and Olive, 1979; Peters and Siefert, 1980; Pitts et al., 1980a), coal fly ash (Jager and Rakovic, 1974; Jager and Hanus, 1980; Korfmacher et al., 1980b; Wehry et al., 1984; Hughes et al., 1980; Blau and Gusten, 1982), silica gel, alumina, carbon microneedles (Barofsky and Baum, 1976), diesel particulates and chromosorb (Eisenberg et al., 1983) and soil (Fatiadi, 1967).

Oxidation products were identified in the photolysis of anthracene, B[a]A, B[a]P, pyrene, perylene and fluoranthene on soot (Tebbens et al., 1971) and on carbon needles (Barofsky and Baum, 1976). Chrysene and coronene photolyzed under similar conditions were stable (Barofsky and Baum, 1976).

In contrast, later work (McCoy and Rosenkranz, 1980) on the photolysis of chrysene (as well as 3-methylcholanthrene) yielded unidentified products that were shown to have increased mutagenetic activities. It was postulated that the mechanism of the photooxidations involved the triplet state of the PAH and singlet molecular oxygen.

A photooxidation mechanism involving singlet molecular oxygen was suggested also (Fox and Olive, 1979) for photolyses of anthracene spiked onto previously collected ambient particulates. The products implicated included anthraquinone, anthrone, bianthryl or the anthracene photodimer. Pitts (1979) also suggested electrophilic attack by singlet molecular oxygen was likely to be an important mechanism in photooxidation of PAH.

Eisenberg et al. (1983) presented evidence consistent with the oxidation of PAH by singlet oxygen according to the following mechanism (where the * indicates an electronically excited species):

$$\text{PAH} + h\nu \dashrightarrow \text{PAH}^* \xrightarrow{O_2} \text{PAH} + O_2^* \dashrightarrow \text{oxy-PAH}$$

Several PAH as well as diesel particulates were found to be efficient singlet oxygen sensitizers. Model compounds (9,10-diphenylanthracene and chrysene) absorbed on Chromosorb 102 reacted in high yield with singlet oxygen to form oxy-PAH products. Similar reactions are likely to occur in the atmosphere. Fatiadi (1967) also postulated the reaction of photoexcited pyrene molecules with adsorbed oxygen.

The reduced photosensitivity, especially of B[a]P, pyrene and anthracenes adsorbed on coal fly ash particles compared to alumina, silica gel or the pure solid (or even PAH in solution), was reported by

Korfmacher et al. (1980a). Taking into account this reduced photosensitivity, presumably resulting from the energetics of surface adsorption, the presence of PAH on coal fly ash particles in the environment would imply long lifetimes. Thus, the persistence of PAH after long range transport of submicron particles is feasible (Blau and Gusten, 1982). Illustrative half-life data for different substrates are presented in Table 5-4.

5.1.1.6 Concentrations of Oxy- and Nitro-PAH in the Atmosphere

The previous discussion has indicated that both oxy- and nitro-PAH may be emitted directly to the atmosphere or may be formed from PAH by reactions in the open atmosphere. There is some evidence that the predominant nitro-PAH are not those related to direct emissions, but, instead, are the result of atmospheric nitration reactions. Observed concentrations in ambient air, then, will reflect contributions from many sources and processes.

Only recently have sampling and analytical methods for PAH derivatives achieved levels of reliability which would allow ambient monitoring data to be accepted with confidence. Thus, historical results ought to be interpreted as qualitative illustrations of compound identifications and atmospheric processes, rather than as quantitative data for exposure estimation purposes. See Davis et al. (1986) and Finlayson-Pitts and Pitts (1986) for discussions of this point.

TABLE 5-4

Half-Lives (in Hours) for the Photolysis of PAH on Different Substrates Determined in the Rotary Photoreactor (Approximately 25 ug of Each PAH/g of Substrate, Except for the Carbon Black)

PAH	Silica Gel	Alumina	Fly Ash	Carbon Black
acenaphthylene	0.7	2.2	44	170
acenaphthene	2.0	2.2	44	a
fluorene	110	62	37	>1000
phenanthrene	150	45	49	>1000
anthracene	2.9	0.5	48	310
fluoranthene	74	23	44	>1000
pyrene	21	31	46	>1000
benz[a]anthracene	4.0	2.0	38	650
chrysene	100	78	38	690
benzo[e]pyrene	70	110	35	>1000
benzo[a]pyrene	4.7	1.4	31	570
perlyene	3.9	1.2	33	870
benzo[ghi]perylene	7	22	29	>1000

[a] Acenaphthene was not originally present on the carbon black studied.

From: Blau and Gusten, 1982.

Both oxy- and nitro-PAH have been identified in the air of Ontario cities (D'Agostino, 1983; Nielsen, 1983; Nielsen et al., 1983a; Ramdahl et al., 1982; Pierce and Katz, 1976; Davis et al., 1986). Systematic studies, however, have not been carried out to allow conclusions about typical, average or peak concentrations.

Table 5-5 shows ranges of measured ambient air concentrations of selected nitro-PAH, for illustrative purposes. It appears from available data that some nitro-PAH are present in concentrations similar to those of many unsubstituted PAH.

The concentrations of oxy-PAH may be comparable to those of B[a]P in highly polluted areas (Konig et al., 1983a). Relationships between the concentrations of PAH and their respective oxidation products, e.g., for B[a]P, B[a]A and their respective quinones, indicate that atmospheric oxidation takes place, especially in summer (Pierce and Katz, 1976).

In other cases, the similar profiles of oxy-PAH in ambient and in source samples show that the sources, in particular diesel exhausts, can account for the presence of oxy-PAH in ambient samples. The absence of oxy-PAH in rural samples, while present in urban samples (Tanner and Fajer, 1983), lends support to urban sources, especially automobile emissions, as major contributors to ambient levels of oxy-PAH.

TABLE 5-5

Ambient Concentrations of Selected Nitro-PAH

Compound[a]	Location[b]	Concentration (ng/m^3)	Reference
1-NP	R	0.02	Nielsen et al. (1983)
	U	0.016	Gibson (1982)
	U[c]	0.031-0.1	D'Agostino (1983)
	R	0.009 ± 0.005	Nielsen et al. (1984)
	U	0.03 - 0.04	Arey et al. (1987)
	U	0.008 - 0.03	Pitts et al. (1985c)
	Re	0.01	Gibson (1986)
	Ru	0.013	ibid.
	S	0.015 - 0.022	ibid.
	U	0.03	ibid.
	I	0.029 - 0.057	ibid.
2-NP	U	0.03 - 0.04	Arey et al. (1987)
	U	0.003 - 0.02	Pitts et al. (1985c)
2-NF	U	0.03 - 0.04	Arey et al. (1987)
	U	0.07 - 0.3	Pitts et al. (1985c)
9-NA	U	0.04	Nielsen et al. (1983)
	R	0.03 ± 0.01	Nielsen et al. (1984)
	U[d]	0.008 - 0.034	D'Agostino (1983)
	U	0.05 - 0.1	Arey et al. (1987)
10-NB[a]A	R	0.01	Nielsen et al. (1983)
	R	0.014 ± 0.007	Nielsen et al. (1984)

Notes:

a) 1-NP = 1-nitropyrene
2-NP = 2-nitropyrene
2-NF = 2-nitrofluoranthene
9-NA = 9-nitroanthracene
10-NB[a]A = 10-nitrobenz[a]anthracene
b) Re = remote
Ru = rural
U = urban
S = suburban
I = industrial
c) May include 8-nitrofluoranthene.
d) May include nitrophenanthrene.

The temporal variability of oxy- and nitro-PAH is likely to be similar to that for the parent PAH. The higher levels seem likely in winter months (due to increased emissions, reduced dispersion and lower chance of thermal and photochemical degradation), but lower levels are likely in summer (although higher ratios of oxy- and nitro-PAH to parent PAH may obtain). Other than data by Pierce and Katz (1976), there are no other data to support the above hypothesis.

Pitts et al. (1982) found that there is a diurnal variation of ambient particulate mutagenicity that is similar to that of primary pollutants, as evidenced by the high correlation of mutagenicity of 3-hour average samples with CO, NO_x and Pb concentrations. The short-term (3 hour average) peak mutagen activities of particles were much higher than the 24-hour average values, but there was agreement between the average of the 3-hour samples and the 24 hour samples. The diurnal variation was not observed in a subsequent study (Pitts et al. 1985c).

5.1.2 Long Range Transport of PAH

The dispersion of pollutants by long range transport is well known for inorganic species, e.g., sulphates, nitrates, and also for organic pollutants such as PAH. Given the common sources of PAH and oxy-PAH, it is expected that long range transport will also be an important factor in determining the distribution PAH and of their oxy- and nitro-PAH products formed during transport.

Mesoscale and long range transport of PAH and oxy- and nitro-PAH have been demonstrated by:

- the presence of PAH at remote sites; and
- profiles (relative abundances) of PAH.

Nielson et al. (1983) showed that mesoscale transport of nitro-and parent PAH were indicated in Riso, Denmark. This was based on comparisons of PAH profiles of ambient samples with those for known sources. Transformation of 1-nitropyrene was thought to be insignificant. In contrast, measurements of B[a]P, 1-nitropyrene and marker inorganic (Pb, Se) and organic (elemental carbon (EC)) species, at near-source and remote sites, in conjunction with back trajectory determination, indicated the formation of 1-nitropyrene during LRT. In fact,the 1-nitropyrene concentrations at the remote site were higher than B[a]P levels at the remote site. Also, the ratio of B[a]P to TSP at the industrial site (near-source) was up to 250 times higher than the B[a]P/TSP ratio at the remote site. The lower B[a]P/marker ratio at the remote site as compared to the near-source sites, is consistent with the reaction of B[a]P during transport, but the disappearance of B[a]P appeared to stabilise in aged aerosols (Gibson and Wolff, 1985). The changing ratio of particle-bound B[a]P/TSP was, undoubtedly, also influenced by the enhancement of vapour-phase B[a]P as TSP concentration decreased due to dispersion.

Daisey and Kreip (1979) also suggested that the Long Range Transport (LRT) of PAH into New York City may be important. The use of B[a]P as a reference compound showed behaviour contrary to the expectation of its rapid degradation by O_3 and HNO_3; thus the ratio of B[a]P to other PAH in ambient samples increased instead of decreased relative to source measurements. The increased ratio was the basis for concluding that LRT under certain meteorological conditions was likely.

Bjorseth et al. (1979) indicated LRT of PAH in Europe, since the concentrations of PAH varied significantly with origin of air masses, and there were correlations of peak levels of PAH with other pollutants (SO_4, soot). The higher winter PAH levels were assumed to be due to less dispersion (lower mixing heights) and a reduced likelihood of photochemical degradation.

Lindskog and Brorstroem (1981) also asserted that the presence of high concentrations of B[a]P was indicative of little chemical degradation, but also used the absence of methylated PAH, together with low concentrations of B[a]P, to support LRT. Similarly, the high correlation of B[a]P concentrations with soot levels together with back trajectories was used to distinguish between local and distant sources.

5.2 Soil

The available information shows that PAH occur in Ontario soils at higher concentrations near a steel mill source (Sault Ste. Marie), near a Toronto highway, as well as in soils and sediments around a coal gasification waste disposal site at Port Stanley, as described elsewhere in this report. Atmospheric deposition through PAH-contaminated rainfall has also been measured in southwestern Ontario. Undoubtedly, PAH occur widely in Ontario soils, and processes of adsorption, biodegradation and possibly volatilization and photolysis influence the fate of PAH in the soil.

5.2.1 Degradation in Soils

Soil microorganisms are capable of metabolizing PAH to varying degrees, as documented in reviews by Radding et al. (1976), Neff (1979), Sims and Overcash (1983) and Bulman et al. (1985). Biodegradation studies have included both measurements of total and specific PAH disappearance rates in soils. The former type of study provides insight into the species responsible for PAH metabolism, while the latter type provides a better indication of "fate" under real world conditions.

Bulman et al. (1985) reviewed the metabolic pathways of PAH degradation. Monooxygenases and dioxygenases are enzymes which catalyze the incorporation of one or two oxygen atoms into the PAH ring structure. The intermediates formed in these pathways undergo further dihydroxylation steps that lead to the eventual cleavage of the aromatic ring and degradation of the resulting phenols and carboxylic acids. Culture studies have also demonstrated that some PAH resistant to biodegradation may be readily degraded in the presence of other PAH which support microbial growth, indicating that these more resistant forms may be cooxidized in PAH mixtures occurring in soils, sediments and sludges.

Several investigators have measured degradation (or perhaps, more accurately, disappearance) rates of PAH in soils, although variations in experimental conditions and analytical techniques have caused problems in defining degradation rates in soil environments. Measured removal rates may also be influenced by the superposition of slow solubilization and desorption rates (i.e., competing physical rate processes). Sims and Overcash (1983) reported half-lives of 3.3 to 175 days for A, 2.5 to 26 days for PHEN, 3 to 35 days for P, 44 to 182 days for F and 4 to 6,250 days for B[a]A. Studies with CHR and B[a]P have reported half-lives as low as 5.5 and 2 days, respectively while other studies have indicated no degradation (Bulman et al., 1985). Gardner et al. (1979) reported degradation half-lives in marsh sediment of 108 to 175 days for A and 105 to 182 days for F. Herbes (1981) reported half-lives of 1.8 and 8.8 days for A and B[a]A, respectively, but no degradation of B[a]P, in pre-exposed sediment downstream from a coking plant discharge. Lee et al. (1984) observed biodegradation of FLN in subsoil near a creosoting plant of 20 to 30% per week. In a study of degradation rates in sediments from a contaminated stream, Herbes and Schwall (1978) measured rate constants (h^{-1}) of 2.5 x 10^{-3}, 1 x 10^{-4} an L 3 x 10^{-5} from A, B[a]A and B[a]P, respectively, while corresponding rates for sediments from an uncontaminated stream were 2.5 x 10^{-4}, 4 x 10^{-6} and L 3 x 10^{-6}. This study indicates that biodegradation proceeds more quickly in acclimated systems, and that larger PAH (4- and 5-ring compounds) are much more resistant to breakdown.

In soil incubation experiments, Bossert and Bartha (1986) found that the biodegradation rate was inversely affected by the number of aromatic rings and directly correlated with water solubility. In this study, 3-ring compounds (A, PHEN and ACEY) were mostly or entirely degraded over four to 16 months, while most of the 4- and 5-ring PAH remained after 16 months of incubation. P which is quite water soluble was an exception; this compound was 97% decomposed after 16 months. Two of the 5-ring compounds, PER and 1,2,5,6-dibenzoanthracene, showed no degradation after 16 months.

While most studies of PAH degradation in soil have assumed that first order kinetics could be used to describe PAH disappearance from soils, Bulman et al. (1985) found that either a model other than first order, or a combination of two different models was required to describe the loss of 99% of PAH from previously uncontaminated soil. PHEN, A, P and F initially disappeared rapidly over 200 days or less until 94 to 98% loss occurred, and rate constants for removal were about the same for both 5 and 50 $mg \cdot kg^{-1}$ concentrations for all compounds except A. Loss of PAH was probably due to complexation with soil particulates since adsorbed fractions reduced the 'free' compound available for analysis. Following the initial loss, the remaining 2 to 6% was lost at a much slower rate. For B[a]A, CHR and B[a]P, only 22 to 88% was degraded over 400 days, and only one kinetic stage was identified for each compound and concentration. Zero order kinetics was appropriate for describing the loss of CHR and B[a]P, leading the authors to conclude that the assumption of first order kinetics in modelling biodegradation of these compounds could seriously underestimate their persistence in soil. Table 5-6 summarizes the half-lives for biodegradation in soil reported by Bulman et al. (1985), along with comparative degradation half-lives compiled from Sims and Overcash (1983).

Sims and Overcash (1983) listed several factors that affect the rate of PAH biodegradation. These include temperature, pH, soil aeration, moisture content, PAH concentration and previous exposure. Degradation tends to increase under conditions ideal for microbial activity. Degradation rate is generally greater at higher concentrations, and is enhanced by previous exposure to the PAH.

TABLE 5-6

A Comparison Half-Lives Calculated on the Basis of First or Zero Order Models from Data Collected by Bulman et al. (1985) with those Reviewed by Sims and Overcash (1983)

PAH	Half Life 5 g/MT added (days)	Half Life 50 g/MT added (days)	Range of Half Lives from Sims and Overcash (days)
First Order			
Phenanthrene	9.7	14	2.5 to 26
Anthracene	17	45	3.3 to 175
Fluoranthene	39	34	44 to 182
Pyrene	58	48	3 to 35
Benzo[a]anthracene	240	130	4 to 6250
Zero Order			
Chrysene	328	224	5.5+
Benzo[a]pyrene	347	218	2+

5.2.2 Sorption

Aqueous concentrations of hydrophobic compounds such as PAH in soils and sediments depend on adsorptive/desorptive equilibria with sorbents (solid particles) within the systems. In soils, liquid-solid partitioning plays a significant role in retarding the migration of PAH in groundwater.

Adsorption may also play a role in PAH degradation through surface-associated chemical and biological processes (McCarty et al., 1981). The affinity of all PAH for soil particles is high, and PAH-sorbent associations are thought to occur primarily through van der Waals forces (Lyman et al., 1982).

The Freundlich adsorption model has been generally applied in evaluating adsorption characteristics of PAH in soil/sediment-water systems. This model is presented as follows:

$$X/M = KC^{1/n}$$

where: X = mass of compound adsorbed from a given mass of solution (ug);
M = mass of solid adsorbent (g);
C = equilibria concentration in the liquid phase (ug/L); and
K,n = empirical constants.

K is a measure of adsorption strength or capacity and $^{1/n}$ is an indicator of intensity, i.e., whether adsorption remains proportional to concentration ($n = 1$), or changes with changing adsorbate concentration ($1 \leq n \leq 3$). When $n = 1$, a linear isotherm results and:

$$S = X/M = KC$$

where: S = concentration in the solid phase (ug/g).

Several studies on adsorption of hydrophobic compounds including PAH have shown that linear adsorption isotherms are appropriate for describing PAH adsorption (e.g., Karickhoff and Brown, 1979; Means et al., 1980; Dzombak and Luthy, 1984). Adsorption coefficients have been reported for many PAH for a variety of soils and sediments. The most important soil and sediment property affecting adsorption is the organic matter content, and adsorption coefficients are frequently reported as K_{oc} values which are normalized for organic matter content. K_{oc} is calculated as K/OC, where K is defined as indicated previously, and OC is the fractional mass of organic carbon in a soil. The implication here is that the degree of adsorption will vary directly with the organic content of the soil. K_{oc} is independent of soil or sediment type, and is a constant for a given chemical. It has been shown that K_{oc} values can be estimated for PAH and many other hydrophobic compounds using the octanol-water partition coefficient (K_{ow}) of the compound based on equations developed by Karickhoff et al. (1979) ($\log K_{oc} = \log K_{ow} -0.21$) and Hassett et al. (1980) ($\log K_{oc} = \log K_{ow} -0.317$). Dzombak and Luthy (1984) examined the application of K_{ow} in prediction of K_{oc} of PAH, and concluded that relationships such as those noted above appear reliable for lower molecular weight PAH, although more experimental K_{ow} and K_{oc} data are required to verify the reliability and scope of these relationships for higher molecular weight PAH.

Typical values for octanol-water partition coefficients of PAH are listed in Chapter 3 of this report. In general, log K_{ow} values range between four and six for PAH, with values tending to increase with molecular weight.

5.2.3 Volatilization

In soils, volatilization is complicated by adsorption and diffusivity. Because most PAH are associated with the solid phase rather than in the aqueous phase in soil, relatively little is available for volatilization. The small fraction for the soil-water interface will have a relatively low potential for volatilization owing to the low Henry's Law constants of PAH.

5.2.4 Photolysis

Little is known of the photoreactivity of sorbed PAH, although there is evidence that adsorption both enhances and inhibits the photochemical breakdown of PAH (Bulman et al., 1985). While it seems reasonable to assume that some photolysis of PAH occurs at the soil surface, this process would be prevented in the subsurface due to the blockage of light penetration. No information was found in the literature that provided insight on the significance of photolysis in the overall fate of PAH in soil systems.

5.3 Water

5.3.1 Abiotic Processes

5.3.1.1 Solubility and Sorption

Due to their low water solubilities, PAH compounds are generally considered to occur in particulate form in lakes and rivers (Herbes, 1977; NRCC, 1983). An equilibrium occurs between the adsorbed and dissolved fractions, and while adsorption is usually favoured, dilute solutions may contain a significant quantity of the dissolved form (NRCC, 1983).

Solubility of PAH in natural waters is affected by several factors. Acenaphthene and pyrene were 24 and 31% less soluble in seawater than in distilled water (Rossi and Thomas, 1981), but salinity effects on PAH solubility are not relevant to most Ontario waters. Solubility tends to increase with temperature over the normal environmental range (May et al., 1978). The NRCC (1983) reviewed molecular properties of PAH that affect solubility. Solubility decreases with increasing molecular weight. Linear PAH molecules tend to be less soluble than angular molecules, and alkyl substitution generally decreases solubility.

A number of different organic compounds have been found to increase PAH solubility in water (NRCC, 1983). They include purines (Weil-Malherbe, 1946), butyric and lactic acids (Ekwall and Sjoblom, 1952), nitrogen-containing organic compounds (Eisenbrand, 1971), acetone, ethanol and dioxane (Suess, 1972).

A recent study by Whitehouse (1985) concluded that "partitioning of PAH into the dissolved phase is significantly influenced by the presence of naturally occurring DOM (dissolved organic material); however, the PAH-DOM interactions are specific with respect to the type of DOM and the compound". Generally, the less soluble PAH were more interactive with DOM, particularly with DOM with a higher molecular weight distribution. McCarthy and Jimenez (1985a, b) similarly found a direct relationship between the hydrophobicity of PAH and the affinity for binding to dissolved humic material (DHM). Gjessing and Berglind (1981) also demonstrated an increase in B[a]P solubility in humic acid-rich water, although Boehm and Quinn (1973) found no effect on phenanthrene and anthracene solubility in sea-water by humic-like organic matter.

Whitehouse (1985) and McCarthy and Jimenez (1985a, b) reported rapid sorption (within minutes) of PAH with organic particles. Karickhoff and Morris (1985), however, showed that more hydrophobic PAH sorbed more strongly, but also more slowly than less hydrophobic compounds; some PAH required days to weeks to reach sorption equilibrium. It may be concluded that adsorption rates may vary considerably with environmental conditions.

PAH also interact with particulate aqueous components, particularly organics. Herbes (1977) demonstrated that a constant fraction (0.45 ±0.01) of total anthracene was adsorbed to 35 mg/L yeast cells over an anthracene concentration range of 0.02 to 31 ug/L. The partitioning of anthracene between dissolved and adsorbed phases was dramatically affected by the concentration of yeast cells with adsorption from 0 to a maximum of 72% at 250 mg particles per litre. Increased temperature resulted in decreased adsorption. The author concluded that 15 to 65% of anthracene would be associated with detrital and living organic matter in natural waters containing moderate levels of suspended organic solids. He also suggested that the role of suspended mineral particulate material may be far less significant in adsorption of PAH than is the role of suspended organic matter, since only 1 to 5% available anthracene adsorbed to montmorillonite clay. Results from Meyers and Quinn (1973) support the last statement, as only 22% of available anthracene adsorbed to bentonite clay. The observed sorption was attributed to van der Waals forces. Sorption of PAH by organic particulates can be predicted using positive correlations between the organic sorption partition coefficient, K_{oc}, and the octanol-water partition coefficient, K_{ow}.

Suspended organic and inorganic particles associated with PAH gradually settle out of the water column. This process is probably the most significant route of PAH removal from water columns (Neff, 1979; Knap and Williams, 1982; Neff, 1985). Suspended sediment transport, however, has been found to be important in the downstream export of PAH in lakes and rivers (e.g., Bahnick and Markee, 1985). Once in bottom sediments, PAH are less subject to a degradative (e.g., photochemical or biological oxidation) or physical (e.g., volatilization) processes. Sediments, therefore, tend to accumulate PAH concentrations by a factor of 1,000 or more relative to the overlying water and can serve as useful indices of the rates of PAH inputs to the aquatic environment (Neff, 1979).

A study conducted by Comba et al. (1985) demonstrated the partitioning of PAH between water and sediment phases in the Detroit River. Table 5-7 shows that low molecular weight hydrocarbons were detected in the water column more frequently than high molecular weight compounds.

TABLE 5-7

PAH in Subsurface Water Samples (ng/L) of the Detroit River (1983)

PAH	Conc. Range (ng/L)	Frequency (20 Stations)
ACEY	5.5-130	3
ACE	3.4-45	7
FLN	8.5-100	9
PHEN	4.7-180	13
A	1.5	1
F	9.5-91	4
P	4.5-11	3
CHR	-	0
B[j or k]F	8	1
B[b]F	-	0
B[a]A	-	0
B[b]CHR	-	0
B[e]P	4.8	1
B[a]P	8	1
PER	3.4-17	2
IN[1,2,3,-cd]P	49	1

From: Comba et al. (1985).

TABLE 5-8

PAH in Suspended Solids (ng/g, dry weight) of the Detroit River (1983)

PAH	Conc. Range (ng/g)	Frequency (13 Stations)
ACEY	120-1800	7
ACE	120-420	3
F	120-2000	4
PHEN	230-1300	2
A	92-770	2
F	180-2800	5
P	180-1900	3
CHR	160	1
B[j or k]F	44	1
B[b]F	44-57	2
B[a]A	76-680	4
B[b]CHR	210-1900	5
B[e]P	22-1400	4
B[a]P	40-4600	6
PER	53-290	2
B[ghi]PER	1.3-5100	8

From: Comba et al. (1985).

TABLE 5-9

PAH in Surficial Sediment Samples (ng/g, dry weight) of the Detroit River (1983)

PAH	Conc. Range (ng/L)	Frequency (16 Stations)
ACEY	750	1
ACE	330-1100	2
FLN	450-520	2
PHEN	500-1800	9
A	370-1300	6
F	1000-4000	10
P	550-4000	10
CHR	1000-5000	6
B[j or k]F	1700-3000	4
B[b]F	560-3000	6
B[a]A	330-2700	7
B[b]CHR	-	0
B[e]P	310-1700	6
B[a]P	600-4900	6
PER	280-370	2
B[ghi]PER	370-810	4

From: Comba et al. (1985)

Conversely, high molecular weight PAH were common in suspended bottom sediment samples (Tables 5-8 and 5-9). Low molecular weight PAH were present in suspended but not bottom sediments. Pore waters from bottom sediments rarely contained any PAH.

Concentrations of aquatic PAH reported by Eadie et al. (1983) for Lakes Erie and Michigan follow a similar pattern of partitioning (Table 5-10 and Figures 5-1 and 5-2) Niagara River data also showed that PAH are generally transported in association with suspended particulates rather than in a dissolved form in the Great Lakes.

5.3.1.2 Volatilization

Low molecular weight PAH with high water solubilities and low partition coefficients, such as naphthalene, phenanthrene and anthracene, are not as highly associated with suspended particles as are higher molecular weight PAH, but are subject to other removal processes such as volatilization (Readman et al., 1984). Henry's law constant, an equilibrium coefficient which describes the distribution between gaseous and aqueous phases, decreases with increasing molecular weight of PAH. Volatilization is also highly dependent on mixing rates within the air and water columns (Southworth, 1979a,b). High molecular weight PAH, such as B[a]P and B[a]A are less prone to volatilization, and were not as sensitive to changes in air and water currents. Southworth (1979a,b) concluded that the rate of vaporization of PAH with four or more rings is relatively insignificant under all environmental conditions. Volatilization losses of lower molecular weight PAH may only be significant compared to other processes in clear, turbulent waters.

TABLE 5-10

Mean PAH Concentrations (ng g^{-1} or ng mL^{-1}) Measured in Lake Michigan Sediment, Pore Water, Dissolved and Particulate Paired Samples

PHEN	A	F	P	CHR	B[a]P	B[ghi]P
Nondepositional Sediments[1] (n = 5)						
90.0	18.4	185.	148.	76.1	62.1	65.7
82.9	2.7	132.	104.	49.8	49.9	61.1
Pore Waters From Nondepositional Sediments (n = 5)						
0.73	0.12	2.02	1.68	2.95	2.32	1.75
0.46	0.036	2.42	1.81	3.52	1.26	-
Depositional Sediments[2] (n = 9)						
836.	195.	1,162.	999.	720.	462.	369.
252.	89.0	357.	319.	338.	266.	362.
Pore Waters From Depositional Sedmiments (n = 9)						
0.43	0.21	0.83	0.82	0.39	0.85	2.67
0.53	0.30	1.29	1.09	0.23	1.26	-
Lake Michigan Suspended Particulate Matter (n = 5)						
2,405.	56.7	4,378.	3,890.	3,678.	2,253.	1081.
2,411.	-	1,768.	1,576.	2,156.	1,954.	-
Lake Michigan Filtered Water (n = 5)						
0.024	0.006	0.015	0.014	0.015	0.014	-
0.025	-	0.009	0.006	0.010	0.008	

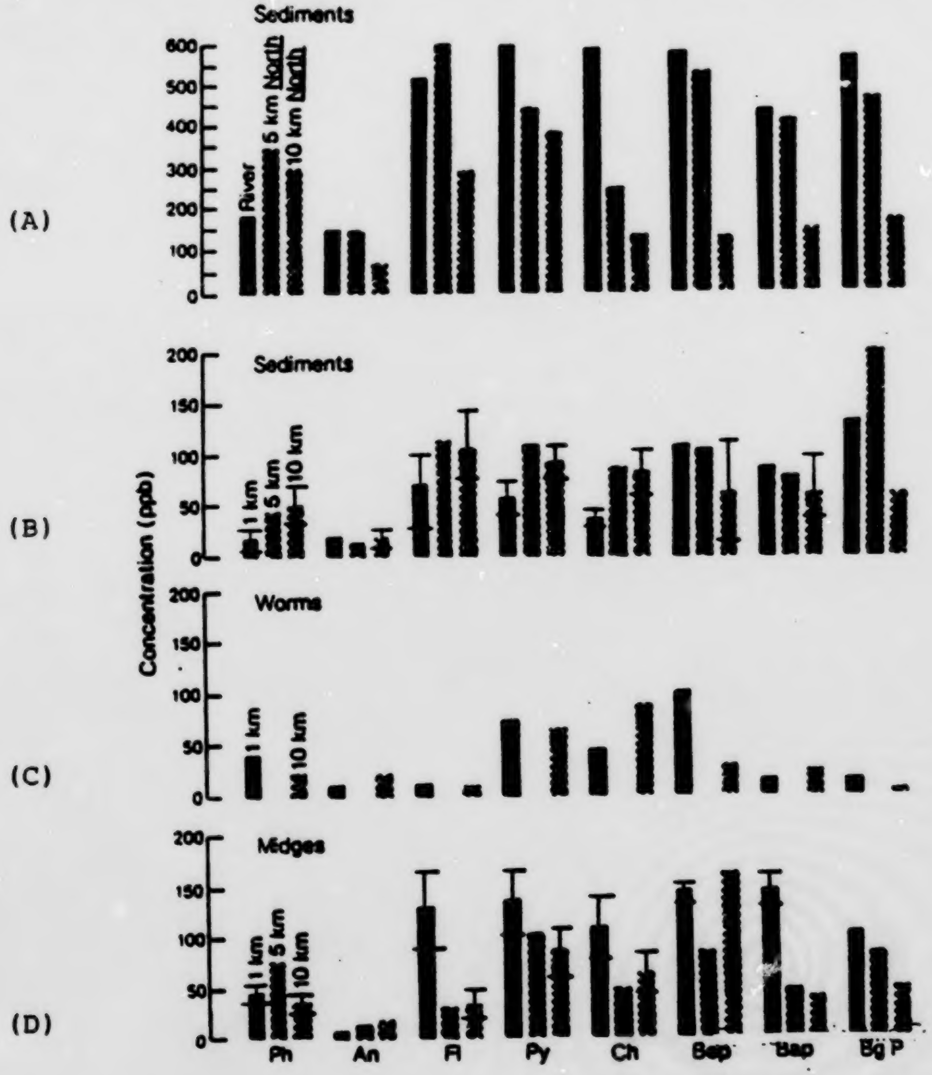
1. Represents near shore sites or non-depositional regions.

2. Was selcted as an area of recent sediment accumulation of deposition.

From: Eadie et al., 1983.

FIGURE 5-1

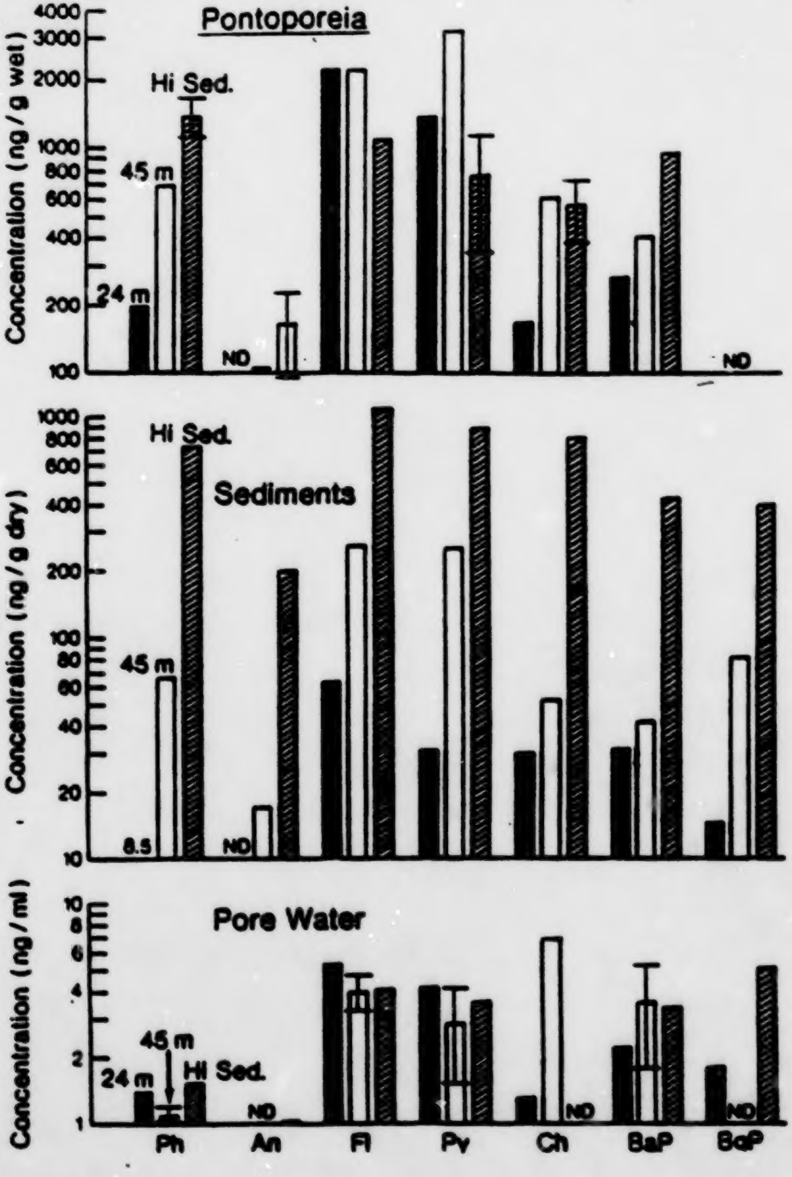
Sediment concentrations of individual PAH in Lake Erie. (A) Mouth of River Raisin 1 km up river of power station, 5 km and 10 km north. (B) Surficial sediments from the remainder of the study area. The bar represents 1 standard deviation from one composite sample and the individual samples. (C) Concentrations in oligochaete worms from 1 and 10 km. (D) Concentration in chironomid midges from 1, 5, and 10 km. Bars represent 1 standard deviation, multiple analyses of a single extract.



From: Eadie et al., 1983.

FIGURE 5-2

PAH concentrations (log scale) in Pontoporeia hoyi (top panel), sediments (middle panel), and pore water (bottom panel) from three stations. Solid bars are data from the 24-m station; open bars are data from the 45-m station. Hatched bars are data from the 60-m deep station in southeast Lake Michigan with high sedimentation rates.



From: Eadie et al., 1983.

Evaporation and sublimation were considered to be major factors in the disappearance of a fluorene from 11 experimental ponds (Boyle et al., 1984). The half-life of fluorene via volatilization from a 1.0-m column was estimated at 100 hours.

5.3.1.3 Photodegradation

The chemical reactions of photo-induced oxidation of aqueous PAH by singlet oxygen, ozone, HO radical, and other oxidizing agents are similar to those involved in photo-oxidation of atmospheric PAH (Neff, 1979, 1985). The formation of endoperoxides is the most common oxidation reaction, with subsequent photolysis or pyrolysis by a free-radical mechanism to form a variety of products (Neff, 1979; cf. Table 5-11). Early photo-oxygenation reactions were often examined in solutions, including a solubilizer and under high oxygen conditions (Nagata and Kondo, 1977; Neff, 1985) (Table 5-12), and may not, therefore, be relevant to dilute aqueous conditions.

Zepp and Schlotzhauer (1979) showed that PAH in pure freshwater or seawater are more likely to undergo direct photolysis than photo-oxygenation. They reported half-lives of 30 to 40 minutes for B[a]P, B[a]A and P, and 21 hours for fluoranthene. Smith et al. (1978) and Southworth (1979a) reported similar half-lives for A, B[a]A and B[a]P of approximately 30 to 35 minutes (Table 5-13). Picel et al. (1985) reported photolysis rate constants of 0.82, 1.0 and 1.4 h^{-1} for P, B[a]A and B[a]P, respectively, in pure water, but rates were six- to nine-fold less in an aqueous coal matrix. Fluoranthene was an exception, with basically no change in photolysis rate between the two solutions.

TABLE 5-11

Free-Radical Oxidation of Some PAH in Air-Saturated Water

Compound	Oxidation Rate ($mole^{-1}$ sec^{-1})	Half-Life
Benz[a]anthracene	5.0×10^3	1.6 days
Benzo[a]pyrene	1.9×10^3	4.3 days
Quinoline	2.8	8 years
Carbazole	29	280 years
Dibenzothiophene	<7.5	>3.5 years

Assumes $[RO_2] = 10^{-9}$ M.

From: Smith et al., 1977; 1978.

TABLE 5-12

Photodegradation of PAH Under Natural Light in Mixed Acetone-Water or Carbon Tetrachloride-Water Solutions

Compound	Degree of Photodegradation (% compound remaining) at 5 hours	10 hours
Anthracene	52.9	32.6
Phenanthrene	57.0	35.9
Benz[a]anthracene	45.5	0.0
Chrysene	96.0	94.0
Fluorene	94.3	91.9
Pyrene	94.6	89.1
Benzo[a]pyrene	93.6	90.5

From: Nagata et al., 1977; Neff, 1985.

TABLE 5-13

Photo-oxidation of Some Dissolved PAH Under Natural Sunlight Conditions

Compound	Rate (sec^{-1})	Half-Life (hours)
Anthracene	3.3×10^{-4}*	0.6
Benz[a]anthracene	3.3×10^{-4}**	0.6
Benzo[a]pyrene	3.6×10^{-4}**	0.5
Carbazole	1.9×10^{-4}**	1.0
Dibenzothiophene	1.5×10^{-6}***	128

* Anthracene in distilled water exposed to mid-day sunlight in mid-summer at a latitude of 35°N (24-h photolysis for mid-summer = 1.2×10^{-4} sec^{-1} and for mid-winter = 4.0×10^{-5} sec^{-1}).

** Instantaneous rate constant for mid-day, mid-summer at a latitude of 40°N.

*** 24-hour rate constant for mid-summer at a latitude of 40°N.

From: Smith et al., 1978; Southworth, 1979a.

Zepp and Schlotzhauer (1979) also reported unusual photochemical behaviour for fluoranthene, which showed an unusually long half-live (above).

Direct photolysis is most important among higher molecular weight, compact PAH, (Zepp and Schlotzhauer, 1979; Neff, 1985) (Tables 5-12 and 5-13). Since light attenuates with depth in the water column, photolysis rates of PAH also decrease. The presence of other materials in the water column (e.g., dissolved or particulate organic substances) can also affect the amount of light reaching PAH by absorbing or reflecting specific wavelengths, or by affecting the mechanism of the photochemical reaction itself (Oliver et al., 1979; Picel et al., 1985a, b, c). Sorption on bottom sediments further decreases photolysis rates (Zepp and Schlotzhauer, 1979; Neff, 1985).

In a field experiment, the half-lives of nine PAH ranged from less than a day to 200 days (Table 5-14), with partitioning between suspended and bottom sediments causing increased persistence (Zepp and Schlotzhauer, 1979). Anthracene disappearance in outdoor channel microcosms was largely due to photolysis with some volatilization losses (Giesey et al., 1983; Bowling et al., 1984). Landrum et al. (1984) reported similar results for anthracene in a stream microcosm,; photolytic degradation to anthraquinone demonstrated to a half-life of 43 minutes.

TABLE 5-14

Direct Photolysis of PAH in a 5 Metre-Deep Inland Water Body[1]

	Sorption Partition Coefficient[2]	Half-Life[3] (days)	
Compound	K_p	No Partitioning[4]	With Partitioning[4,5]
Phenanthrene	180	59	69
Anthracene	160	4.5	5.2
9-methylanthracene	550	0.8	1.2
Fluoranthene	280	160	200
Pyrene	400	4.2	5.9
Benz[a]anthracene	1,500	3.7	9.2
Chrysene	4,200	13	68
Naphthacene	3,800	0.2	1.0
Benzo[a]pyrene	3,100	3.2	13

[1] Suspended sediment concentration, 20 $mg \cdot L^{-1}$; diffuse attenuation coefficient, 11 m^{-1}.

[2] K_p computed from octanol-water partition coefficients.

[3] Integrated over full summer day, latitude 40°N.

[4] No partitioning assumes that PAH are completely in the water column and the photolysis rates are affected only by light attenuation.

[5] With partitioning describes rapid exchange between the top centimetre of the bottom sediment and the water column. This exchange could involve continual sedimentation and resuspension of the top layer of the bottom sediment.

From: Zepp et al., 1979.

5.3.2 Biological Processes

5.3.2.1 Bioavailability and Bioaccumulation

The presence of PAH in the tissues of various aquatic organisms indicates that organisms are able to accumulate PAH at low concentrations from ambient media and food (Neff, 1985). Fish, invertebrates, insects and algae located near large sources of PAH have demonstrated tissue levels in the ng/g to ug/g range (cf. Eadie et al., 1982a, b; Knutzen and Sortland, 1982; Pruell et al., 1984), while biota from remote or relatively unpolluted areas contain non-detectable levels to concentrations in the low ng/g range as presented in Tables 5-15 and 5-16 (Brown and Pancirov, 1979; Murray et al., 1981). The accumulation of PAH in aquatic organisms is due to the highly hydrohobic/lipophilic nature of most PAH causing the chemicals to partition into lipid stores in the organism (Neff, 1985). Accumulation is the net of the processes of uptake, metabolism and depuration or excretion.

The partitioning of PAH in the aquatic environment (e.g., adsorbed, dissolved, complexed with DOM) may affect the extent to which biota take up ambient PAH. McCarthy et al. (1985) tested the bioavailability of B[a]P, B[a]A and A in the presence of dissolved humic material (DHM). High hydrophobicity was positively correlated with sorption to DHM and resulted in reduced availability for uptake by Daphnia magna. B[a]P uptake by oysters was reduced in the presence of DOM (Fortner and Sick, 1985).

TABLE 5-15

Range of Polycyclic Aromatic Hydrocarbon Concentrations (ug/kg, wet weight) in Bivalve Shellfish from Different Oregon Bays

Bay	Site	Species	PAH Concentration	Degree of Industrialization
Tillamook	TIM	M. edulis	40-60	Relatively pristine.
Tillamook	TSS	M. arenaria	30-60	Relatively pristine.
Tillamook	TBC	C. gigas	35-45	Relatively pristine.
Yaquina	Y140	C. gigas	30-45	Relatively pristine.
Coos	C3S	M. arenaria	70-90	Relatively pristine near highway.
Coos	C11G	T. capax	30-110	Light; nearby marinas; fish processing plant.
Coos	CSS	M. arenaria	480-650	Heavy; shipping docks; wood products industry, marinas.
Yaquina	YIM	M. edulis	140-440	Light shipping docks.
Yaquina	Y2M	M. edulis	675-1,325	Heavy; marinas, fish processing plants, recreational development.

From: Mix, 1984.

TABLE 5-16

Average Polycyclic Aromatic Hydrocarbon Concentrations (ug/kg., wet weight) in Mussels

	Type of Site (number of sites)					
	Clean (8)		Urban (12)		Industrial (6)	
PAH	Mean	Range	Mean	Range	Mean	Range
Phenanthrene	17.2	7-33	17.7	4-43	214.0	28-621
Fluoranthene	22.4	2-85	46.1	6-198	215.3	8-476
Pyrene	15.8	2-78	43.8	5-158	199.7	7-540
Benzo[a]pyrene	7.1	1-13	38.3	2-236	101.2	5-329

From: Mackie et al. (1979).

Leversee et al. (1983) reported decreased accumulation of B[a]P by D. magna in water containing humics, but anthracene and dibenzoanthracene uptake were unaffected. The results were confirmed for B[a]P in the same study in the presence of natural organics from surface waters of South Carolina. Uptake of B[a]P by bluegills (Lepomis macrochirus) was reduced by 90% in water with DHM. Naphthalene uptake was not changed by DHM, but naphthalene is a low molecular weight PAH with a low binding affinity for DHM. Anthracene and phenanthrene uptake by the amphipod Pontoporeia hoyi were not altered by DHM, but B[a]P, B[a]A and P were less bioavailable (Landrum et al., 1985).

Neff (1984a) demonstrated that PAH sorbed to sediments and suspended particles were less bioavailable to aquatic organisms. Availability was directly related to the compound solubility and sediment grain size, while inversely related to organic carbon concentration and animal size. Since sediments may contain high concentrations of adsorbed organic pollutants, he concluded that they represent an important source of contaminants to organisms despite their lower bioavailability. Varanasi et al. (1985) also concluded that not all B[a]P bound to sediments was bioavailable to a variety of estuarine organisms.

Only limited data are available on PAH concentrations in aquatic biota occurring in the open environment in Ontario. A survey of contaminant concentrations in Great Lakes sport fish was conducted by Zenon (1985). Seven to twenty (20) fish per lake were tested for ten PAH levels. While most PAH were non-detectable in the majority of samples, residues were measured as high as 110 ng/g (phenanthrene in brown bullhead from the St. Lawrence River). Most other maximum reported residues were less than 50 ng/g. Corresponding water concentrations were not tested, so the degree of bioaccumulation cannot be estimated. Konasewich (1978) also reported PAH in Great Lakes fish, but the levels were not quantified. Lake trout from Lake Superior and burbot from Lake Huron contained phenanthrene and alkylated phenanthrene above the detection limit of approximately 0.01 to 0.5 ug/g. PER, B[k]F, B[a]P and COR were measured in carp and pike fillets from Hamilton Harbour contained the greatest concentrations, particularly of B[a]P and COR (up to 0.4 ug/g), while Detroit River fish had levels that were generally below 0.05 ug/g and were often undetectable.

Fish do not appear to accumulate PAH to the extent of aquatic invertebrates, probably due to the ability of the former group to metabolize hydrocarbons (Eisler, 1987). Elevated levels of a hepatic enzyme related to hydrocarbon metabolism, aryl hydrocarbon hydroxylase (AHH), have been measured in lake trout inhabiting the industrialized area of western Lake Ontario (Luxon et al., 1987). Roubal et al. (1978) suspected that higher BCFs for PAH in flounder than in coho salmon was related to differences in AHH activity rather than to differences in lipid content.

PAH are metabolized relatively rapidly by fish. Linder and Bergman (1984) reported a BCF of 200 for rainbow trout relative to a 36 ug/L exposure concentration of A after an 18-hour exposure. In the following 96 hours, A was rapidly metabolized and eliminated, but metabolism proceeded quicker during the 8-hour dark phase of a photo cycle, indicating that PAH metabolism may vary diurnally. Radio-labelled B[a]P was taken up by northern pike through the gut and gill, and possibly through the skin, was metabolized in the liver and subsequently excreted in bile and urine (Balk et al., 1984). Eight and one-half days after the initial exposure, most of the radioactivity was in the form of PAH metabolites. Spacie et al. (1983) reported half-lives A and B[a]P of 17 and 67 hours respectively, in bluegills. The BCFs relative to water were 900 and 4,900 for A and B[a]P, respectively, and were lower than predicted, due to rapid metabolism of the compounds.

A table of bioconcentration factors (BCFs) measured under controlled conditions for a number of PAH was compiled by Eisler (1987) (Table 5-17). Values differ widely between species, and seem to be dependent on a number of factors (discussed below). Generally, algae, molluscs and other species which are incapable of metabolizing PAH show greater accumulation. Increases in the molecular weight of PAH, K_{ow}, exposure time and the lipid content of the organism are some factors which tend to encourage bioaccumulation (Eisler, 1987).

PAH uptake by two benthic invertebrates (Pontoporeia hoyi and Mysis relicta) were examined by Frez and Landrum (1985). Both represent an important food source to some Great Lakes fish, but demonstrated significant differences in uptake and depuration of B[a]P, A and Phen. In addition, seasonal variation occurred. Increased water temperature and decreased PAH solubility enhanced uptake in M. relicta, while uptake and depuration were unaffected by PAH solubility in P. hoyi. The PAH half-life in P. hoyi is approximately four times greater than that in M. relicta. Jovanovich and Marion (1985) similarly demonstrated that anthracene uptake and depuration in clams increased with temperature, but concluded nutritional status and reproductive stage play a minor role in anthracene accumulation. Varanasi et al. (1985) concluded that factors such as feeding strategy and excretion rates probably account for higher B[a]P bioaccumulation in amphipods than in clams.

TABLE 5-17

PAH Bioconcentration Factors (BCF) for Selected Species of Aquatic Organisms

PAH compound, organisms and other variables	Exposure period[a]	BCF
ANTHRACENE		
Cladoceran, Daphnia magna	60 m	200
Fathead minnow, Pimephales promelas	2 to 3 d	485
Cladoceran, Daphnia pulex	24 h	760 to 1200
Mayfly, Hexagenia sp.	28 h	3,500
Rainbow trout, Salmo gairdneri	72 h	4,400 to 9,200
9-METHYLANTHRANCENE		
Cladoceran, Daphnia pulex	24 h	4,583
BENZ[a]ANTHRACENE		
Cladoceran, Daphnia pulex	24 h	10,109
BENZO[a]PYRENE		
Teleosts, 3 spp., Muscle	1 h to 96 h	0.02 to 0.1
Clam, Rangia cuneata	24 h	9 to 236
Bluegill, Lepomis macrochirus	4 h	12
Atlantic salmon, Salmo salar Egg	168 h	71
Midge, Chironomus riparius, larvae	8 h	166
Rainbow trout, liver	10 d	182 to 920
Oyster, Crassostrea virginica	14 d	242
Northern pike Esox lucius		
Bile and gallbladder	3.3 h	3,974
"	19.2 h	36,656
"	8.5 d	82,916
"	23 d	53,014
Liver	3.3 h	259
"	19.2 h	578
"	8.5 d	1,376
"	23 d	619
Gills	3.3 h	283
"	19.2 h	382
"	8.5 d	372
"	23 d	213
Kidney	3.3 h	192
"	19.2 h	872
"	8.5 d	1,603
Other Tissues	3.3 h to 23 d	< 55
Mosquitofish, Gambusia affinis	3 d	930
Bluegill		
No dissolved humic material (DHM)	48 h	2,657
20 mg/l DHM	48 h	225
Cladoceran Daphnia magna	6 h	2,837
Alga, Oedogonium cardiacum	3 d	5,258
Periphyton, mostly diatoms	24 h	9,600
Mosquito, Culex pipiens quinquefasciatus	3 d	11,536
Sand sole, Psettichthys melanostictus		
Egg	6 d	21,000
Snail, Physa sp.	3 d	82,231
Cladoceran, Daphnia pulex	3 d	134,248

TABLE 5-17 (cont'd)

PAH Bioconcentration Factors (BCF) for Selected Species of Aquatic Organisms

PAH compound, organisms and other variables	Exposure period	BCF
PERYLENE		
Cladoceran, *Daphnia pulex*	24 h	7,191
PHENANTHRENE		
Clam, *Rangia cuneata*	24 h	32
Cladoceran, *Daphnia pulex*	24 h	325
PYRENE		
Cladoceran, *Daphnia pulex*	24 h	2,702
Rainbow trout, liver	21 d	69

a) m = minutes, h = hours, d = days

Reproduced from: Eisler, 1987.

Uptake of B[a]P, A, PHEN and P by an oligochaete, Stylodrilus heringianus, were measured in water and sediment from Lake Michigan (Frank et al., 1985). Half-lives in the organisms were generally less than two days. Uptake rate constants were similar to those of P. hoyi, but depuration rates were more comparable to M. relicta. The authors concluded that PAH fate in S. heringianus was more dependent on metabolic rate than on any particular property of the PAH.

Pittinger et al. (1985) conducted an in situ experiment in Virginia to measure bioaccumulation of Phen, F, P, B[a]A+Chr, BF and B[a]P by oysters relocated from a non-impacted site to an urban/industrial area. PAH increased from 0 to as much as 11.7 ppm dry weight within three days, then stabilized. Depuration occurred to non-detectable levels after oysters were transferred to pristine waters. Levels in indigenous oysters corresponded with degree of industrial and urban development and shipping traffic in the habitats.

Water solubility was related to depuration rates of PAH in contaminated lobsters from Sydney, Nova Scotia (Uthe and Musial, 1986). Approximately 85% of F was lost from the digestive glands over one year, while as little as 6% of Chr (less water soluble) was lost. In an earlier study, Uthe et al. (1984) measured more rapid depuration of PAH from digestive glands of lobsters (31 to 77% over five weeks), but uptake of the PAH had also occurred over a shorter period of time. Lobsters exposed to a diesel oil spill in Newfoundland for less than ten hours contained significantly higher concentrations of PHEN and P over controls (Williams et al., 1985).

Gerould et al., (1983) measured bioconcentration of anthracene in the midge Chironomus riparius, and found that the BCF was more strongly affected by differences in biotransformation rate due to temperature than by differences in uptake rate.

Landrum and Scavia (1983) investigated the influence of sediment on anthracene uptake, depuration and biotransformation by the amphipod Hyallela azteca. The mean uptake rate constant for waterborne A was the same in the presence or absence of sediment. Sediment-associated A (i.e., sorbed and in pore water) was estimated to contribute 77% of the steady-state equilibrium burden of H. azteca. The role of sediment B[a]P in the uptake by P. hoyi was variable, but deemed to be important to the body burden when in high concentrations (Landrum et al., 1983).

The prediction of BCFs for compounds in mixtures may be difficult using single compound kinetics. For example, tissue accumulations of radiolabelled B[a]P in the oyster, Crassostrea virginica, were not affected by the simultaneous presence of naphthalene and PCBs (Fortner and Sick, 1985), while exposure of rainbow trout to anthracene alone resulted in higher BCFs than when they were exposed to A in oil shale retort water (Linder et al., 1985). The retort water was believed to either decrease the bioavailability of A to the fish, or limit the transport of contaminants from uptake sites to storage and processing sites. The authors concluded that prediction of BCFs for complex mixtures may be difficult based on single compound kinetics. In addition, contaminants in mixtures may act as inhibitors to PAH metabolism, thereby affecting extent of bioaccumulation.

PAH are also accumulated by fish eggs and larvae. Solbakken et al. (1984) observed uptake of Phen and B[a]P in coastal cod, Gadus morhua, eggs and larvae after 24 hours of exposure. The degree of uptake appeared dependent on the molecular weight and the lipiophilic characteristics of the contaminants.

The uptake of PAH by fish can be related to sediment concentrations, particularly for bottom-dwelling species (Connor, 1984). Fish/sediment ratios for a specific compound in different areas were correlated with the residence time of the water in that area (e.g., lakes had higher ratios than well-flushed coastal areas). The author proposed that predictions of BCFs from sediment concentrations would reduce variability stemming from water concentration data, but employing the model for non-bottom-dwelling fish would also result in a ten-fold increase in variability. A similar experiment by Landrum and Scavia (1983) resulted in overestimates of BCFs for benthic organisms, based on the water concentration of anthracene. Since 77% of the body burden was derived from sediment contaminants, sediment-associated anthracene must have been less bioavailable. They also proposed that BCF estimations be based on sediment concentrations for benthic organisms.

For several years, researchers have attempted to relate contaminant uptake by organisms to various physical properties of the compound, such as solubility or the octanol-water partition coefficient (K_{ow}). A number of these relationships have been developed, based on a wide variety of organic contaminants including PAH. Table 5-18 presents some observed BCFs for various PAH against their predicted values.

TABLE 5-18

Observed Versus Predicted Bioconcentration Factors for Selected PAH

PAH	Species	Log K_{ow}	Water Solubility (ppm)	Equation (based on log K_{ow} or WS)	Observed	Predicted	Reference
Phen	*Chlorella fusca* (algae)	4.46, 4.57		log Bf (1 day, wet wt) = 0.681 log K_{ow} + 0.164	1,760	1,590	Geyer *et al.* (1984)
A	*Chlorella fusca* (algae)	4.54		log Bf (1 day, wet wt) = 0.681 log K_{ow} + 0.164	1,760	1,800	Geyer *et al.* (1984)
Phen	*Pontoporeia hoyi* (amphipod)		1,002	log BCF = 2,791 - 0.564 log WS	19,173	617	Eadie *et al.* (1983a)
A	*Pontoporeia hoyi*		0.0446	log BCF = 2,791 - 0.564 log WS	16,667	3,571	Eadie *et al.* (1983a)
F	*Pontoporeia hoyi*		0.206	log BCF = 2,791 - 0.564 log WS	79,696	1,507	Eadie *et al.* (1983a)
P	*Pontoporeia hoyi*		0.132	log BCF = 2,791 - 0.564 log WS	44,175	1,939	Eadie *et al.* (1983a)
Chr	*Pontoporeia hoyi*		0.0018	log BCF = 2,791 - 0.564 log WS	20,280	21,829	Eadie *et al.* (1983a)
B[a]P	*Pontoporeia hoyi*		0.0002	log BCF = 2,791 - 0.564 log WS	55,000	75,374	Eadie *et al.* (1983a)
A	*Lepomis macrochirus* (bluegill)	4.46		log BCF = 0.85 log K_{ow} - 0.70	900	1,209	Spacie *et al.* (1983)
B[a]P	*Lepomis macrochirus*	6.06		log BCF = 0.85 log K_{ow} - 0.70	4,900	28,230	Spacie *et al.* (1983)

5.3.2.2 Biodegradation

Bacteria initially metabolize PAH by incorporating the oxygen atoms of molecular oxygen into the PAH structure to form a cis-dihydrodiol. Oxidation reaction occur with further enzymatic action to form catechols and eventually CO_2 and water. Mammalian oxidation enzymes (monooxygenases) metabolize PAH by forming reacting arene oxides then a trans-dihydrodiol. It appears that some fungi also metabolize PAH to trans-dihyrodiols with an enzyme system similar to mammalian monooxygenases (Gibson et al., 1975; Cerniglia et al., 1982; Neff, 1985).

The evaluation of the importance of biodegradation of PAH in the open environment is difficult due to the number of factors which influence degradation rates.

Variations in the type of PAH present, the structure of the microbial community, environmental conditions, and the method of assessment have led to extreme variations in reported biodegradation rates (Oudot, 1984). Reviews of the subject generally conclude that PAH are degraded more rapidly in aerobic than anaerobic conditions.

Also, the higher molecular weight PAH are more resistant to biodegradation. Microorganisms which were previously adapted to PAH are able to metabolize PAH more readily than unexposed organisms. PAH which are resistant to degradation may be metabolized more readily in the presence of other, more easily degraded PAH (NRCC, 1983; Neff, 1985).

Oudot (1984) examined biodegradation of bulk Arabian light crude oil by a microbial culture over 60 days. The aromatic hydrocarbons degraded approximately 50%. Degradation rates for each compound were related to the number of rings in the molecule, decreasing in the order 1 > 3 > 2 > 4 > 5 rings. In an experiment using oil in water and sediments from the North Sea, Massie et al. (1985) also showed that microorganisms have the potential to degrade smaller PAH rapidly in the water column and in surface sediments. B[a]P mineralization was tested in sediments only, and was found to be minimal.

Biodegradation of PAH in activated sludge was investigated by Freitag et al. (1985). The conversion of PAH to CO_2 was 0.3% and 39.6% for A and Phen, but less than 1% of the 4- and 5-ring PAH (B[a]P, Per, B[a]A and DB[a,h]A) were mineralized to CO_2.

There is controversy in the literature concerning the effect of suspended solids on degradation rates. Hall et al. (1986) found that no significant microbial degradation of ACE occurred when no suspended solids were present. Degradation was significantly more rapid in the highest concentration of one suspended sediment sample tested over the next lowest concentration after seven days. In the presence of a different sample of suspended sediment with a higher organic content, significant degradation of A also occurred, but was not related to the concentration of the suspended sediment. It should be noted that the behaviour of naturally occurring suspended solids may be different from that of experimentally re-suspended sediments.

Herbes (1981) suggested that the larger 5-ring PAH were less biodegradable in sediments due to their strong sorption to sediment particles and resultant reduced availability. Comparative half-lives of six PAH in water and sediment in a stream are presented in Table 5-19.

TABLE 5-19

Degradation Rate Constants (k) and Half-Lives (t 1/2) for Mixed Bacterial Populations in Water and Sediment from the Same Stream

	Sediment		Water	
	$k(h^{-1})$	t 1/2	$k(h^{-1})$	t 1/2
Anthracene	1.6×10^{-2}	43 h	2.0×10^{-3}	350 h
Benz[a]anthracene	3.3×10^{-3}	208 h	ND	
Benzo[a]pyrene	3.4×10^{-4}	83 h	ND	
Dibenz[a,h]anthracene	1.2×10^{-4}(1)	166 h	ND	

ND = not detectable

(1) single determination

From: Herbes, 1981.

Other studies of biodegradation in soils and sediments have shown that while biodegradation does occur in the aquatic environment, the rate of metabolism is dependent on many environmental factors as well as the composition of the microbial community and the PAH composition.

5.3.4 Microcosm Studies

The intentional contamination of artificial ecosystems, or microcosms, has been widely practiced in studies of contaminant transport and fate. Microcosm studies of some PAH have been conducted to determine the fate of each compound and the relative importance of various environmental compartments and fate.

Fluorene was applied to experimental pond ecosystems at concentrations of 0.12 to 10.0 mg/L (Boyle et al., 1984). Fluorene at concentrations above the limit of solubility appeared to sublime from the pond surface. Fluorene disappearance was rapid and attributed largely to evaporation and sublimation as well as sedimentation and degradation. Seven days after treatment, only a small fraction of applied fluorene was accounted for (7 to 18%). The half-life of F1n in the 0.12-mg/L pond was 6.7 days, while at the highest application concentration (10.0 mg/L) the half-life was 27.4 days.

Anthracene added to an artificial stream microcosm also rapidly disappeared (Landrum et al., 1984). Anthracene was rapidly photolyzed to anthraquinone (half-life 43 minutes) which was subsequently rapidly photolyzed. The organic sediment acted as a major repository, absorbing 0.2% of the 14-day input dose. Periphyton took up 0.04% of the applied dose, and all other compartments (water and biota) contained relatively minor amounts.

Another channel experiment with anthracene provided similar results (Bowling et al., 1984). Anthracene was input at 15 ug/L continuously for 36 days. Downstream dissipation was rapid via photolysis, during daylight. Some loss was attributed to volatilization. Aufwuchs achieved maximum concentrations within 4 days (BCF = 1260) but the concentration relative to the total input was only 0.02%. After discontinuing A input, background concentrations were achieved in water and aufwuchs within 24 hours and 72 hours, respectively.

In a closed model aquatic ecosystem, B[a]P was applied to water at 0.002 mg/L (Lu et al., 1977). Bioaccumulation was observed for three days in organisms from several trophic levels. BCFs for fish, alga, mosquito, snail and daphnia were 930, 5,258, 11,536, 82,231 and 134,248 respectively.

Labelled B[a]A was introduced to a large-scale marine microcosm resembling shallow coastal waters of the northeastern U.S. (Hinga et al., 1980). All B[a]A and breakdown products were removed from the water with a half-life of 52 hours. Most B[a]A was rapidly transferred to sediments. Some ^{14}C activity was observed in particulates and plankton with an initial half-life of 35 hours. After 230 days, 29% of the applied radioactivity had been respired to CO_2, while the remaining activity was evenly divided between parent compound and intermediate metabolic products.

6.0 ENVIRONMENTAL LEVELS AND SOURCE CONTRIBUTIONS

The purpose of this chapter is to integrate information from several chapters to describe typical concentrations of PAH which may be found in Ontario in media through which environmental exposure to PAH may occur. Emission profiles and emission rates are used to estimate the relative contributions of selected source categories to the atmospheric loading of PAH in Ontario. Finally, summary conclusions regarding an assessment of the information contained in the report are offered.

6.1 Levels in Air, Soil and Water

Ambient air PAH levels near the Niagara River were measured in a study by the Atmospheric Environment Service (Hoff and Chan, 1987). Hi-vol samples were collected at three (3) sites during 1982 and 1983. Sampling sites were at the following locations:

- Niagara-on-the-Lake;
- Fort Erie; and
- Niagara Falls.

The sampling configuration was a filter followed by a polyurethane foam (PUF) plug. The two fractions represent nominally, the particle and vapour portions. Because of blow off and volatilization processes, the particle fraction may be distorted for intermediate molecular weight PAH. The sum of the two fractions is more accurate.

Average particulate and gaseous PAH concentrations from the three sites are summarized in Tables 6-1 and 6-2 for tests conducted in September 1982 and January 1983 respectively. The results showed a strong, local influence of heavier weight particulate PAH from the winter sampling period (January, 1983).

For example, in ambient air, the PAH concentration was highest at Fort Erie, lower at Niagara Falls and lowest at Niagara-on-the Lake, which is directly related to the inputs from industry and mobile sources (Hoff, 1987). An examination of wind flow direction during the sampling period indicated a strong influence on the PAH level arising from emissions from the urban areas of Buffalo, Niagara Falls, NY, and Niagara Falls, Ontario, for easterly winds. In addition, the increase in PAH emissions at Niagara-on-the-Lake for north northwesterly winds was possibly due to transport from the Toronto-Hamilton urban corridor.

Ontario Ministry of the Environment annual PAH results for the period 1973 to 1983 at the Niagara Falls sites are illustrated in Figure 6-1 along with results of the AES study (Hoff and Chan, 1987).

A definitive study was carried out by Katz et al., 1978, on the PAH distribution in the ambient air of four (4) Ontario cities, i.e., Toronto, Hamilton, Sarnia and Sudbury. Two sites in Toronto were reported. Selected results from the various sampling sites are summarized in Tables 6-3 and 6-4.

The study shows that the highest PAH levels occurred at the Hamilton site, followed by Toronto, Sarnia and Sudbury. B[ghi]PER was reported at significant levels at all the sites. The likely source was postulated to be from the exhaust gases of motor vehicles.

A recent survey of ambient air PAH has also been carried out in Toronto from 1984-1986 (Dann, 1988). Data are presented in Table 6-5.

TABLE 6-1

Mean Ambient Air Levels of Polycyclic Aromatic Hydrocarbons at Niagara-on-the-Lake, Niagara Falls and Fort Erie in September, 1982

Compound	Filter concn. n	Filter concn. pg m^{-3}	PUF concn. n	PUF concn. pg m^{-3}
Phenanthrene	5	180 ± 140	5	4800 ± 1100
Pyrene	3	65 ± 53	5	300 ± 350

n = number of samples

From: Hoff and Chan, 1987.

TABLE 6-2

Mean Ambient Air Levels of Polycyclic Aromatic Hydrocarbons Near Niagara-on-the-Lake, Niagara Falls and Fort Erie in January, 1983

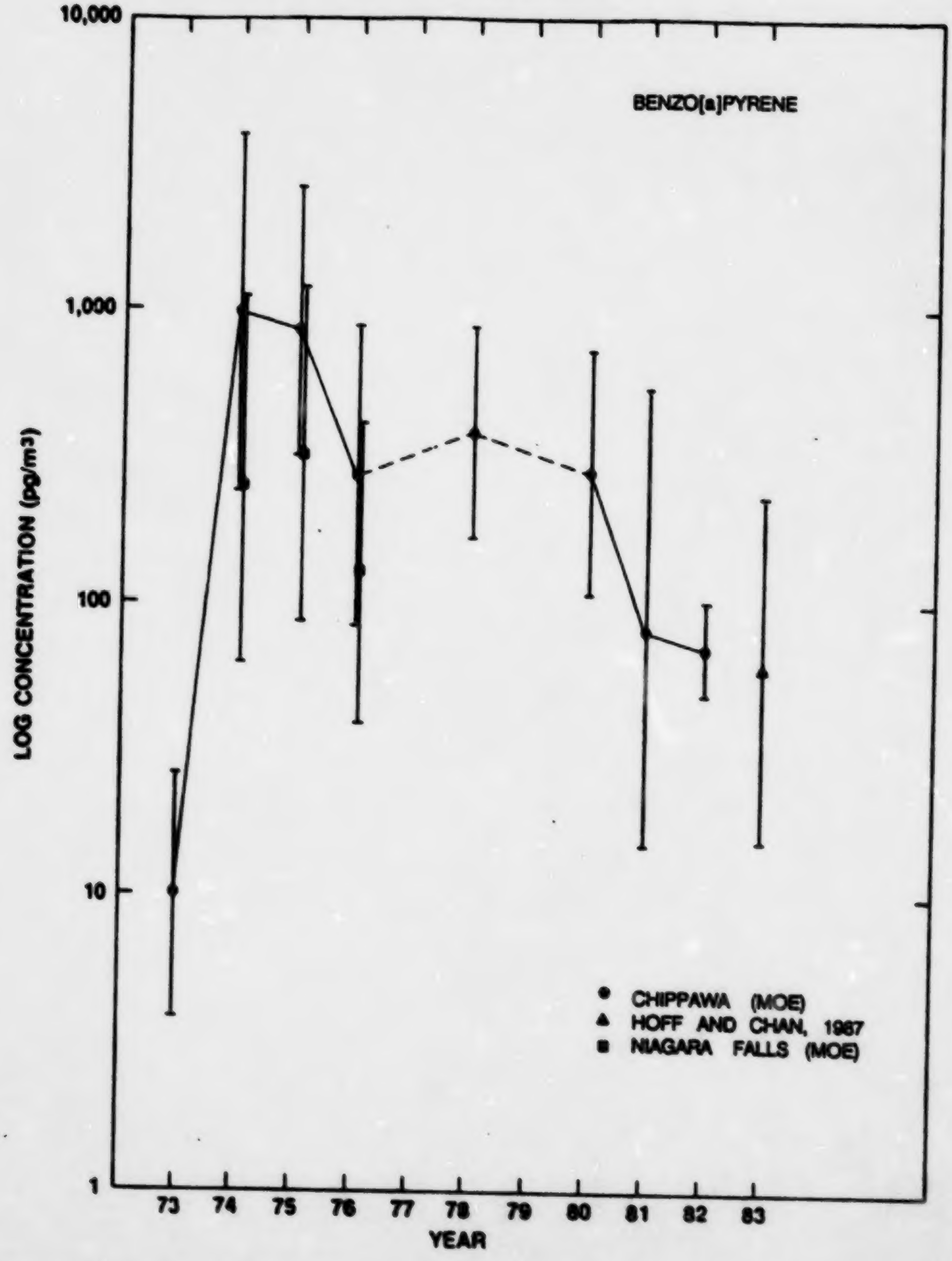
Compound	Filter concn. n	pg m^{-3}	PUF concn. n	pg m^{-3}
Phenanthrene	19	830 ± 1000	16	13000 ± 5900
Anthracene	19	45 ± 57	9	990 ± 960
Fluoranthene	19	1400 ± 1900	9	3700 ± 2200
Pyrene	19	1200 ± 1800	8	3000 ± 2100
Benz[a] anthracene	19	2800 ± 5600		bdl
Benzo[j] + benzo[k] fluoranthene	18	1100 ± 1500		bdl
Benzo[e]pyrene	17	230 ± 440		bdl
Perylene	11	23 ± 52		bdl
Benzo[ghi] perylene	12	530 ± 1500		bdl

n = number of samples
bdl = below detection level

From: Hoff and Chan, 1987.

FIGURE 6-1

Graphical Illustration of Benzo[a]pyrene Concentration and Year of Study at Chippewa/Niagara Falls in the Particulate Phase



From: Hoff and Chan, 1987.

TABLE 6-3

Particle-Bound PAH Concentration Ranges in Ambient Air Measurements for 4 Ontario Cities

PAH Concentration

PAH	Toronto		Hamilton		Sarnia (S)		Sudbury	
	(ug/g)	(pg/m^3)	(ug/g)	(pg/m^3)	(ug/g)	(pg/m^3)	(ug/g)	(pg/m^3)
Benzo[a] pyrene	5.9-20.2	408-1674	9.6-50.6	1404-3498	2.4-11.4	114-596	2.6-15.3	111-444
Benzo[e] pyrene	4.9-15.6	375-1294	4.2-54.4	606-3771	1.1-11.5	52-603	0.7-13.6	23-317
Benzo[b] fluoranthene	8.4-20.7	693-1829	5.6-113.1	813-7841	5.2-17.9	243-938	4.1-27.6	173-650
Benzo[k] fluoranthene	4.3-11.1	285-916	2.9-74.2	419-5145	1.3-8.4	70-439	1.7-11.6	57-271
Perylene	0.4-2.3	51-193	1.0-5.8	141-403	0.3-1.7	13-87	0.4-2.1	17-50
Benzo[ghi] perylene	50.5-127.2	3303-10528	39.9-108.7	5809-7532	16.8-51.7	1038-2700	23.9-128.7	779-3009

From: Katz et al., 1978.

TABLE 6-4

Total Particle-bound Concentrations of 10 PAH in the Ambient Air of Four Ontario Cities April 1975-March 1976* Seasonal Means

	PAH Concentration									
	Toronto		Toronto		Hamilton		Sarnia		Sudbury	
Sample Period	pg/m^3	ug/g	pg/m^3	ug/g	pg/m^3	ug/g	pg/m^3	ug/g	pg/m^3	ug/g
Apr.-June	9,161	102.4	8,303	109.8	9,851	67.8	3,749	60.6	2,013	61.6
Jul.-Sept.	9,838	113.7	5,496	84.1	17,582	126.5	1,706	36.5	1,663	39.5
Oct.-Dec.	17,360	209.7	8,535	140.2	32,152	463.9	6,123	117.1	3,780	169.3
Jan.-Mar.	7,855	100.8	17,491	127.8	15,084	180.4	2,090	76.8	5,169	221.1
Mean	11,053	131.6	9,956	115.5	18,667	209.6	3,417	72.7	3,156	122.9

From: Katz et al., 1978.

* Includes the following PAH in addition to the six listed in Table 6-3.

dibenz[def,mno]chrysene
naphtho[1,2,3,4,def]chrysene
benzo[rst]pentaphene
dibenzo[b,def]chrysene

TABLE 6-5

Summary of Mean Total PAH Concentrations (ng/m^3) in Toronto (October 1984 - July 1986 - 42 Sampling Days)

Compounds	Mean Concentration
Acenaphthylene*	4.12 ± 5.98
Acenaphthene*	2.24 ± 2.04
Fluorene*	5.51 ± 4.37
2-Methyl-Fluorene	3.66 ± 2.34
Phenanthrene	15.64 ± 8.68
Anthracene	1.60 ± 2.85
Fluoranthene	4.91 ± 2.70
Pyrene	3.87 ± 2.88
Benzo[a]Fluorene	0.53 ± 0.48
Benzo[b]Fluorene	0.27 ± 0.27
1-Methyl-Pyrene	0.18 ± 0.21
Benzo[ghi]Fluoranthene	0.49 ± 0.69
Benzo[a]Anthracene	0.40 ± 0.92
Chrysene & Triphenylene	0.73 ± 0.58
7-Methyl-Benzo[a]Anthracene	0.00 ± 0.00
Benzo[b&k]Fluoranthene	1.26 ± 1.45
Benzo[e]Pyrene	0.48 ± 0.60
Benzo[a]Pyrene	0.30 ± 0.52
Perylene	0.04 ± 0.11
Indeno[1,2,3-cd]Pyrene	0.46 ± 0.62
Dibenzo[a,c]&[a,h]Anthracene	0.04 ± 0.09
Benzo[b]Chrysene	0.04 ± 0.13
Benzo[ghi]Perylene	0.07 ± 1.16
Anthanthrene	0.02 ± 0.05
Total PAH	47.57 ± 27.26

* Collection efficiency poor and dependent on ambient temperature (see text).

From: Dann, 1988.

Although useful for general information, the data presented in the preceding tables do not provide a link between source emissions and ambient air data. Outside of Ontario, there are some examples which associate source emissions with ambient air data: Daisey et al. (1981; 1986); Daisey (1985); Thrane and Wikstrom (1983).

Whereas all the authors admit that any attempt to conduct source apportionment receptor modelling for PAH will probably leave many unanswered questions because of the lack of accurate information and because of the reactivities of PAH, Daisey and Kneip (1981) have attempted to group the emissions from six (6) sources and report in terms of the B[a]P/B[ghi]PER ratios. Her group have also attempted source apportionment receptor modelling for PAH (Daisey, 1985).

It has also been noted in various sections of the report that B[a]P/B[e]P, Anthn/B[e]P, B[ghi]PER/B[e]P ratios as well as B[k]F, coronene, nitropyrene or retene levels may be indicative of certain sources. No unambiguous picture emerges from the data, however, because of the severe temporal and spatial varaiability of relative concentrations of PAH in ambient air samples. In the absence of unique source PAH markers, it is not possible to apply receptor modelling to obtain quantitative source apportionment except in specific local situations, where long-term studies might establish an adequate database to resolve PAH source contributions. Inorganic (elemental) source and receptor sample profiles will undoubtedly provide better data than PAH or other organic composition with which to attempt source apportionment, for the near future.

6.2 Residue Levels in Ontario Soils

The results from soil evaluation in the Port Credit and Oakville/Burlington areas, which formed part of a site decommissioning program undertaken by Texaco and Shell, showed anthracene present in one sample, and phenanthrene, benz[a]anthracene and chrysene, benzo[b&k]fluoranthene in 7 to 8 samples (Golder Associates, 1987).

The following PAH were detected in a large number of the soil samples analyzed.

- Pyrene (15 samples), mean concentration of 0.13 ppm with a standard deviation of 0.15 ppm;
- Fluoranthene (16 samples), mean concentration of 0.15 ppm with a standard deviation of 0.20 ppm; and
- Benzo[a]pyrene (28 samples), mean concentration of 0.024 ppm with a standard deviation of 0.034 ppm.

6.3 Residue Levels in Sediments

PAH levels in surface waters has been reported by the Great Lake Environmental Research Laboratory on all Great Lakes (Table 6-6). A compilation of PAH data of domestic water sources is available in Table 6-7 for the city of Erie, based on samples collected in 1976 (Eadie et al., 1982; IJC, 1978). Concentrations in raw lake water are typically below 1 ug/L, and often below detection limits. The data indicate that average concentrations of PAH in filtered lake water are typically below 0.1 ug/L.

TABLE 6-6

PAH Concentrations in Surface Water (Filtered) Surficial Sediments, Sediment Porewater and Benthos from the Great Lakes

	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benzo[a]pyrene
Water[1]						
n = 6						
Mean	0.024	0.006	0.015	0.014	0.014	0.012
s	0.025	0.006	0.009	0.006	0.010	0.008
Surficial Sediment (ppb dry): range/n						
Superior (n = 1)	34	-	88	53	-	28
Michigan (n = 10)	6-1,268	-	9-1,664	8-1,430	-	4-944
Huron (n = 3)	11-272	-	33-487	36-256	-	23-294
Erie (n = 4)	18-431	-	65-285	57-287	-	56-173
Ontario (n = 5)	40-205	-	210-1,000	56-1,182	-	76-306
Surficial Porewater (ppb):						
n = 9						
Mean	0.43	0.21	0.83	0.82	0.39	0.85
s	0.53	0.30	1.29	1.09	0.23	1.26
Bulk Sediment (ppb dry)	84	-	30	22	14	69
60 um and Finer Sediment (ppb dry)	192	-	440	343	322	242
and Oligochaetes (ppb wet) (Lake Erie near shore)	185	-	190	250	130	20

[1] Filtered lake water.

From: Eadie et al., 1982a.

TABLE 6-7

PAH Data for Erie, PA (Finished Water)

	Concentration (ng/L)	Detection Limit (ng/L)
Fluoranthene	ND	10
Benzo[k]fluoranthene	A	
Benzo[b]fluoranthene	ND	30
Benzo[ghi]perylene	ND	50
Benzo[a]pyrene	ND	30
Indeno[1,2,3-cd]pyrene	ND	50

ND - not detected
A - analysis was not attempted

From: IJC, 1978.

Additional data on suspended sediment concentrations for the Great Lakes are available for the Niagara River (Table 6-8). Concentrations in suspended sediments in the Niagara River range between 4 to 16 ppb for ACEY to about 100 to 1,500 ppb for A/PHEN, F, P, CHR/B[a]A, B[b,k]F and B[a,e]P.

Additional data on PAH levels in surficial sediments in the Great Lakes basin are presented for all Great Lakes (Table 6-6), Hamilton Harbour (Table 6-9), and the St. Lawrence River (Tables 6-10 and 6-11). Data from Eadie et al. (1982a; Table 6-6) indicate that most PAH in surficial sediments are associated with the solid phase rather than pore water, and that PAH are preferentially associated with fine fractions.

Sediment core data for PAH in the Great Lakes demonstrate the presence of greater levels of contamination in the surficial layer than in deeper deposits. Table 6-12 provides a list of PAH profiles found in sediment core off Toronto (IJC, 1976). Core profiles of PAH and alkylated PAH at varying distances from the Niagara River mouth further demonstrate this surface contamination phenomenon, and illustrate the direction of PAH transport from the Niagara River (Onuska et al., 1983).

6.4 Residue Levels in Fish and Wildlife

Data on PAH concentrations in tissues of fish from the Great Lakes basin are provided in Tables 6-13 and 6-14. Concentrations in fish flesh for individual PAH are typically in the ppb range.

TABLE 6-8

PAH Concentration in Suspended Sediments: Niagara-on-the-Lake

PAH	Concentration (ppm)
Acey	0.004 to 0.016
Ace	0.008 to 0.038
Fln	0.010 to 0.042
A/Phen	0.166 to 1.58
F	0.173 to 0.942
P	0.141 to 0.824
Chr/B[a]A	0.105 to 1.51
B[b and k]F	0.193 to 1.08
B[a and e]P	0.190 to 1.10

From: Canada Ontario Review Board, 1981.

TABLE 6-9

Polynuclear Aromatic Hydrocarbons in Hamilton Harbour Sediments 1982

Compound	Range (ug/g)*
Fluoranthene	1.9 - 4.3
Perylene	1.2 - 9.7
Benzo[k]fluoranthene	1.1 - 9.0
Benzo[a]pyrene	1.2 - 11.1
Benzo[ghi]perylene	1.6 - 8.6
Indeno[1,2,3-cd]pyrene	1.1 - 9.7

* Number of samples = 6

From: MOE, 1985.

TABLE 6-10

Mean, Minimum and Maximum Values of PAH (ng/g) in Sediments from 30 Stations in the St. Lawrence River, 1981

	PAH Concentration		
	Mean	Minimum	Maximum
PAH Total	551.5	31	1,883
Anthracene + Phenanthrene	32.0	2	960
Fluoranthene	120.0	11	360
Benz[a]anthracene	53.0	4	120
Benzo[b]fluoranthene	130.0	7	770
Benzo[k]fluoranthene	46	3	130
Benzo[g,h,i]perylene	70	2	190
Indeno[1,2,3-cd]pyrene	68	2	900

From: IJC, 1987a.

TABLE 6-11

PAH in St. Lawrence River Sediment Samples Collected in the Vicinity of the General Motors Facility at Massena, New York

	Concentrations (mg/kg, dry weight)	Number of Samples Out of 8 in Which Compound Detected
Acenaphthene	BMDL	2
Anthracene	BMDL to 1.01	2
Benz[a]anthracene	BMDL to 4.00	5
Benzo[a]pyrene	4.32 to 6.55	2
Benzo[b]fluoranthene	1.72 to 7.92	5
Benzo[ghi]perylene	BMDL to 2.02	3
Benzo[l]fluoranthene	2.94 to 4.37	2
Chrysene	BMDL to 4.57	5
Dibenz[a,h]anthracene	BMDL	2
Fluoranthene	BMDL to 3.64	7
Fluorene	BMDL	5
Indeno[1,2,3-cd]pyrene	BMDL to 3.74	3
Naphthalene	BMDL	1
Phenanthrene	BMDL to 4.16	6
Pyrene	BMDL to 2.78	6

BMDL - below minimum detection limit

From: IJC, 1987a.

TABLE 6-12

Abundances of Polycyclic Aromatics in Lake Ontario Sediment (Latitude 43°39', Longitude 78°12') (ug/g dry sediment)

	0-5 cm	10-15 cm	20-25 cm	30-35 cm	55-60 cm	70-75 cm
Biphenyl	0.014	0.007	0.009	0.004	0.004	
Tetrahydropyrene	0.056	0.029	-	-	-	-
Fluoranthene	0.281	0.058	-	-	-	-
Pyrene	0.056	0.029	-	-	-	-
Chrysene/ Triphenylene	0.225	0.088	0.052	-	-	-
Dimethyl chrysene	0.112	-	-	-	-	0.018
Benzo[b]fluoranthene	0.450	0.029	0.017	0.034	0.010	0.009
Methyl benzofluoranthene	0.056	-	-	-	-	-
Benzpyrenes	0.337	-	0.017	0.034	0.010	0.009
Perylene	0.056	0.029	0.017	0.034	0.30	0.046
Methyl benzpyrene	0.056	-	-	-	-	-
20-methyl cholanthrene	0.337	-	-	-	-	0.018
Benzperylene	0.225	-	-	-	-	-
Coronene	0.562	-	-	-	-	-
Total	2.935	0.269	0.112	0.089	0.084	0.131

- no data

From: IJC, 1976.

TABLE 6-13

Highest PAH Values Recorded in Fish Collected from the Great Lakes

Lake (Total No. of Samples)	Maximum PAH (ng/g)									
	Acey	Ace	Fln	Phen	A	F	P	Chr	B[a]A	B[a]P
Ontario (20)	33.0 (20.0)	22.0 (30.0)	20.0 (25.0)	110.0 (55.0)	6.0 (40.0)	70.0 (45.0)	32.0 (40.0)	1.8 (20.0)	6.5 (20.0)	3.2 (5.0)
Erie and St. Clair (7)				4.3 (14.3)		1.0 (14.3)	0.3 (14.3)			
Huron (12)	43.0 (8.3)	18.0 (16.7)		54.0 (33.3)	8.3 (25.0)	43.0 (33.3)	9.5 (25.0)			
Superior (11)		12.0 (18.2)	20.0 (36.4)	33.0 (45.5)	5.8 (36.4)	17.0 (45.5)	4.0 (45.5)	5.9 (36.4)	4.9 (36.4)	4.9 (9.1)

Numbers in parantheses indicate frequency of detection.

From: Zenon, 1985.

TABLE 6-14

Polynuclear Aromatic Hydrocarbons in Great Lakes Fish Identified by Mass Spectrometry

	Hamilton Harbor		Detroit River	
PAH	Carp	Pike	Carp	Pike
acenaphthene		x		x
fluorene	x		x	
anthracene	x	x		x
phenanthrene	x	x		x
1-methyl phenanthrene	x	x		x
1-methyl anthracene	x	x		x
2-methyl anthracene	x	x		x
2-methyl phenanthrene	x	x		x
9-methyl anthracene				x
fluoranthrene		x	x	x
pyrene	x	x		x
1,2-benzofluorene	x		x	
2,3-benzofluorene	x		x	
chrysene	x	x		x
benzo[a]pyrene		x		x
perylene		x		x
dibenz[a,h]anthracene	x	x		x
coronene	x	x		x

x detected

Other compounds scanned for but not found inlude 1-methyl pyrene, benzo[e]pyrene, anthantrene, benzo[ghi]perylene and dibenz pyrenes.

From: IJC, 1978.

The only recorded data on PAH concentrations in wildlife tissues (other than fish tissues) available for the Great Lakes area are provided by Hallett et al. (1977), who reported several PAH in herring gull lipids from samples collected in the Lake Ontario basin (Table 6-15). Because PAH concentrations were generally lower than those reported in fish, it was concluded that food chain bioconcentration did not take place. Since that study, no further analyses have been reported on Great Lakes gull tissues (Canadian Wildlife Service, pers. comm.).

6.5 PAH in Human Tissues and Fluids

PAH have been demonstrated to accumulate in human tissue. Concentrations of 9 target PAH were determined in human fat and liver samples from 10 normal people with uncharacterized smoking habits, occupation and residence (Cobana et al., 1981). Benz[a]anthracene and dibenz[a,h]anthracene were not detected in either tissue type. Total (of 7 remaining target) PAH concentrations average 1100 pg/g in fat and 380 pg/g in liver. Concentrations of benzo[a]pyrene ranged from <5-59 pg/g in fat, from 10-32 pg/g in liver; concentrations of benzo[b]fluoranthene ranged from 56-260 pg/g in fat, from 33-88 pg/g in liver.

Concentrations of 4 target PAH determined in human bronchial carcinoma tissue demonstrated benzo[a]pyrene to be the most significant PAH, with values ranging from 0.3-15,000 ng/g (Tomingas et al., 1976). Several PAHs (acenaphthene, fluorene, phenanthrene, anthracene and pyrene) have also been detected in human atherosclerotic aortas, in concentrations of 8-30 ng/g (Ferrario, 1985).

TABLE 6-15

Identification of Polynuclear Aromatic Hydrocarbons in Great Lakes Herring Gull Lipid

Compounds	Concentration (ug/kg) Pigeon Island	 Kingston	Mass Spectra Confirmation
acenaphthene	0.038	0.007	-
fluorene	0.044	0.003	-
anthracene	0.152	0.024	+
phenanthrene	nd	0.002	+
2-methyl phenanthrene	0.021	0.007	+
1-methyl phenanthrene	0.010	0.015	+
9-methyl anthracene	0.011	0.025	+
fluoranthrene	0.082	0.017	+
pyrene	0.076	0.015	+
1,2-benzofluorene	a	a	+
2,3-benzofluorene	a	a	+
chrysene	0.053	a	+
benz[e]pyrene	0.026	0.021	+
benzo[a]pyrene	0.038	0.030	+
perylene	0.053	0.026	+

From: Hallett et al., 1977

a = PCB interference; b = standards of compounds unavailable, compounds identified by mass spectra; nd = not detected.

Other compounds scanned for but not found inlude 1-methyl pyrene, benzo[e]pyrene, anthantrene, benzo[ghi]perylene and dibenzopyrenes.

The milk of nursing mothers who smoke has been found to contain benzo[a]pyrene in concentrations of 7.6-387 mg/L (average 129.5 mg/L) (Health & Welfare Canada, 1979). There were no comparable data on non-smoking nursing mothers.

6.6 Trends in Levels and Source Contributions

Although specific estimates of trends in PAH emissions in Ontario are not available, projections for surrogate pollutants may be used to estimate trends in total (but not individual) PAH emissions from some sources.

For example, tighter controls on industrial point source emissions of particulate matter, which are being instituted now and which are projected to become more stringent under the proposed Ontario Clean Air Program (CAP), will reduce emissions of particle-bound PAH. Projections of the provincial emission inventory of particulate matter from combustion sources, then, should predict the total PAH emission trend for the future. Based on such a qualitative analysis, the major PAH emission sources in Ontario identified in Chapter 3 are likely to behave as follows.

It is unlikely that the incidence of forest fires in Ontario will change significantly over the next few years. Therefore, it is reasonable to assume that PAH emissions from this source will remain constant for a ten to twenty year planning period.

Vehicle emissions of PAH may be assumed to decrease significantly as more of the fleet is equipped with 3-way converters. Although vehicle emission control standards are becoming more stringent, projected increases in the number of vehicles and annual distance travelled per vehicle will probably counterbalance the decreasing unit emissions. A decrease is projected over the next ten years, but an increase will occur after that, which leads to the conclusion that PAH emissions could be at present levels at the beginning of the next century. This trend is predicted for vehicle NO_x emissions (R. Salmon, Environment Canada, conference presentation, February 1989).

Estimates of residential fuel wood future consumption in Ontario are not available. It seems reasonable to assume, however, that the increased use of fuel wood which would be implied by increased population in the province will not materialize, for several reasons. The escalating price of fuel wood because of scarcity of supply near urban areas, and the apparent trend toward fewer detached homes being built in urban areas would imply a lower per capita fuel wood utilization rate, at least in southern Ontario. Emission factors may be further reduced by tighter specifications on residential woodburning equipment or regulation of the use of such equipment (as now occurs in New England and the Pacific Northwest of the U.S.) during air pollution episodes. No specific information is available about regulatory plans in either of these areas in Ontario. It may be assumed, then, that PAH emissions from residential woodburning in Ontario will decrease from estimated current levels, but there is no rational basis for estimating this trend quantitatively.

Control programs for coke oven emissions in Ontario and improved process technology at newer facilities have reduced particulate (therefore PAH) emissions from existing plants significantly over the past fifteen years. PAH emissions from coke ovens would be expected to decrease in conjunction with particulate emissions. If the best available technology and best available control technology have already been applied to coke ovens in Ontario, then it is reasonable to expect that only modest emission reductions will be achieved in the near futue. In this case, emissions from coke ovens in Ontario will be related to future production levels. In the absence of quantitative estimates of future production or controls, it is reasonable to assume continuation of coke oven emissions at apporoximately their current levels, for the purposes of regulatory assessment of PAH.

The qualitative picture which emerges from the foregoing is a relative decrease in importance of residential woodburning as a source of PAH in Ontario, the other major sources identified remaining constant.

Two of the minor sources of PAH identified - municipal incineration and coal-fired power plants - are and will be subject to particulate matter emission control programs and, therefore, are not expected to increase and may decrease in importance relative to other types of sources. The recent banning in Ontario of incinerators in apartment buildings has eliminated that source of PAH emission.

Air monitoring data indicate qualitative trends which have occurred between the mid-1970's and mid-1980's, at selected sites in Ontario. The data presented in Tables 6-3 to 6-7 and 6-10 and in Figure 6-1 show that typical B[a]P levels in Toronto and Niagara, for example, have decreased from about 1 ng/m^3 annual average to about 0.1 to 0.3 ng/m^3 over similar ten-year monitoring periods. The Toronto data are for two separate periods about 10 years apart. Comparing the Toronto data of Katz et al (1978) with those of Environment Canada (Dann, 1988), average concentrations of other PAH have also decreased between 1975/6 and 1984/6. For example, the annual mean concentrations of B[e]P, a chemically stable PAH present almost exclusively in particulate matter, decreased from about 0.75 to about 0.5 ng/m^3 over that period of time. The seasonal maximum (in fall) concentration of B[e]P decreased from 1.3 ng/m^3 in 1975/6 to 0.6 ng/m^3 in 1984/67. B[ghi] Per decreased dramatically from an annual average of about 7 ng/m^3 in 1975/6 to 0.8 ng/m^3 in 1984/6. Thus, various PAH have exhibited reductions in concentration with time to differing degrees, but all major PAH have decreased, according to the very limited data available. The two studies cited above as the basis for comparisons in Toronto used different sampling, extraction and analytical techniques, but there is no reason to believe that the results are not comparable. These results are consistent with downward trends observed elsewhere (Dann, 1988), but data are so fragmentary that calling the existing evidence a trend is not appropriate.

7.0 HUMAN EXPOSURE LEVELS (DIETARY AND LIFESTYLE SOURCES)

PAH are widespread in the environment, and various PAH have been demonstrated to be carcinogenic. Therefore, attempts have been made to quantify human exposures to PAH, and to assess the relative importance of sources and exposure pathways. One reviewer (Santodonato et al., 1981) estimated human exposure to total PAH in North America to average 1.8-16.2 ug/day, from the inhalation of ambient air (0.207 ug/day), the ingestion of drinking water (0.027 ug/day) and the ingestion of food (1.6-16 ug/day).

B[a]P was estimated, by the same reviewer, to constitute approximately 10% of the total PAH including naphthalenes; estimates of the percentage contribution of other carcinogenic PAH were incomplete, due to lack of data. It can be seen from these estimates that food is considered a major source of PAH exposure, that there is a high degree of variability in the exposure estimate, and that the role of carcinogenic PAH, other than B[a]P, in total human exposure has not been well characterized.

Note also that lifestyle factors which contribute to total PAH exposures, such as smoking or the use of pharmaceuticals/cosmetics containing PAH were not included in these estimates.

The following section addresses these issues. The objective of this section is to review the available data, as well as recent and current work which contribute to an understanding of human exposures to PAH in Ontario. Where data specific to Ontario are lacking, other relevant data are cited.

7.1 PAH in Ontario Food

The occurrence of PAH in unprocessed foods may be the result of external deposition, uptake, or biosynthesis. PAH contamination of unprocessed seafoods is the result of rapid uptake from water, and accumulation in crustaceans and bivalves (Uthe and Musial, 1986). A recent review of PAH in the terrestrial environment (Edwards, 1983) indicated that most PAH contamination of vegetation is by direct deposition from the atmosphere; that surface-to-mass ratio (relative leaf area) is a dominant factor in PAH accumulation; that some plants in some growing conditions can take up PAH and may translocate and/or concentrate specific PAH in other plant parts; and that concentrations of PAH are generally greater on plant surfaces, such as peelings, than in internal tissues. For example, the accumulation of 20 PAH in lettuce showed a positive gradient with proximity to a busy highway, whereas the levels in rye did not (Larsson, 1985a). Vegetables such as kale, with larger surface areas and a longer growing season, accumulate higher levels of PAH than other foodstuffs (Vaessen et al., 1984) (Grimmer, 1982; Edwards, 1983).

Bush beans grown in laboratory conditions were shown to assimilate and translocate PAH from roots to leaves and stems, as had soybeans, ryegrass, alfalfa, chick pea, and cucumbers in earlier work (Edwards, 1985; Edwards, 1983); but the effects of variables, such as PAH molecular weight, solubility in water, physio-chemical form in the substrate, and plant species differences are not yet clear. Nonetheless, PAH concentrations in peeled onions, beets, oranges and apples have been shown to be much lower (an order of magnitude) than concentrations in the peels (Edwards, 1983; Grimmer, 1982).

The occurrence of PAH in processed or cooked foods may be the result of combustion fumes, formed in hot smoking processes and in the generation of heat during grilling processes, reaching the surface of the food. Endogenous formation of PAH on the surface of food subjected to high temperatures (e.g., frying or electrical broiling) does not appear to cause appreciable increases in PAH concentrations (Larsson et al., 1983). Factors affecting PAH levels in hot smoked foods include the smoking process (type of fuel, air flow, combustion temperature), smoke generation techniques, smoke treatment (cleaning) techniques, and smoking time. Factors affecting PAH levels in grilled foods include the type of fuel, distance between food and heat source, cooking temperature, cooking time, and fat content of food being grilled (Larsson, 1985b). For example, beef patties containing 30% fat and grilled over hickory wood were found to contain 16 PAH in total concentration of 68 ug/kg of meat; the same beef cooked over mesquite wood (from the southwest U.S.) was found to contain 24 PAH in total concentration of 549 ug/kg of meat (Maga, 1986). Similarly beef containing 10% fat had half the total PAH concentration of the 30% fat beef. Barbecue briquets (coal-based and wood charcoal) available to the Canadian consumer in the mid-1980s were found to contain total PAH concentrations of 2.5 to 13 ug/g of briquet, and contained 30-53 individual PAH in various samples (Kushwaha et al., 1985). There were no data describing PAH compositions of combustion fumes, or of PAH concentrations in food cooked over these briquets.

PAH in smoked foods (and likely in grilled foods as well) are concentrated in the outer layer. For example, skin from smoked herring had total PAH concentrations 4-24 times higher than those in the flesh; as well, the projection of high molecular weight PAH was higher in the skin (Larsson, 1985b). Therefore, higher concentrations will likely be found in products or portions with higher surface-area-to-weight ratio.

7.1.1 Analysis of PAH in Foods

Although this is probably a minor source of PAH in food, the potential for PAH migration from food packaging material is not known. However, PAH have been observed in some petroleum and synthetic waxes used in food packaging (Sheraishi et al., 1975; Howard et al., 1965). Concentrations of total PAH exceeded 0.1 ppm in 2 of 32 waxes analyzed (Howard et al., 1965); B[a]P was observed in average concentrations of 2.9 and 4.6 ppb in petroleum and synthetic wax respectively (Sheraishi et al., 1975).

There have been several surveys to determine numerous PAH in Canadian foods. Those involving a variety of food types have been carried out by the Food Research Division, Health Protection Branch, Health and Welfare Canada (Lawrence and Das, 1986; Lawrence and Weber, 1984a, b; Panalaks, 1976). Foods were purchased from local retail and fast food outlets in Toronto and Ottawa. Samples were digested with alcoholic KOH, followed by partitioning into solvents such as cyclohexane or isooctane; interferences were removed by solvent partitioning and column chromatography on silica gel, Florisil or Sephadex LH-20. Analyses were done by high pressure liquid chromato-graphy (HPLC) - fluorescence detector (Lawrence and Weber, 1984b), or UV and fluorescence detectors (Panalaks, 1976) with some confirmation by gas chromatography - mass spectrometry/selected ion monitoring (GC-MS/SIM) (Lawrence and Das, 1986; Lawrence and Weber, 1984a). Recoveries typically averaged 60-75%, although there were ingredients of much lower recoveries. Results were not corrected for recoveries.

The results are summarized below. Where concentrations of total carcinogenic PAH are given, the totals refer to the sum of individual PAH analyzed which are considered to be carcinogenic (U.S. EPA, 1987).

1. Leafy vegetables included swiss chard, cabbage, romaine lettuce, local spinach, and imported spinach (Lawrence and Das, 1986). They contained the lowest levels of PAH in the foods analyzed. No PAH were detected in any chard, cabbage or lettuce. Only fluoranthene was found (32 ng/g) in one spinach (3 samples) in concentrations of 0.1-0.5 ug/kg.

2. There are no Canadian data, and little other data on PAH in fruits. One review cited B[a]P concentrations of 0.5-30 ug/kg in fruits (IARC Vol. 32).

3. Charbroiled hamburgers from four different retail outlets contained total (of 8 target) PAH in concentrations of 1.8-37.7 ug/kg (Lawrence and Das, 1986). Concentrations of carcinogenic (6 target) PAH were 1-21 ug/kg, and constituted 47-69% total PAH. Dimethylbenzanthracene, B[a]P and DB[ah]A constituted over half the total carcinogenic PAH.

   Comparisons of PAH types and concentrations in charbroiled and fried hamburgers from commercial outlets (Lawrence and Weber, 1984a), demonstrated the effect of the cooking process - of 18 target PAH, 5 or fewer were observed in fried hamburgers, with total PAH of up to 1.3 ug/kg; whereas 10-14 were observed in charbroiled hamburgers, with total PAH of approximately 35 ug/kg. Concentrations of carcinogenic PAH also increased from 0.3 ug/kg to 14 ug/kg.

There are almost no other data on PAH levels in other (unsmoked) meats cooked by conventional oven or stove-top methods. Other charcoal broiled meats (steak, pork chops, chicken) were observed to contain up to 6 (of 9 reported target) PAH, with total PAH concentrations in the range of 5-55 ug/kg (Panalaks, 1976).

4. Smoked meat products, including bologna, frankfurters, salami, sausages, bacon, hams, beef and pork were found to contain up to 5 (of 11 target) PAH in some samples of each food type, at maximum levels of 0.2-8 ug/kg (Panalaks, 1976). Of the 5 most frequently observed PAH in this group of samples, 4 are carcinogenic.

   More recent work done on smoked cheese, poultry, pork and beef products in the U.S. (Joe et al., 1984) demonstrated the presence of 8 PAH (of which 5 are carcinogens) of 12 target PAH in most of the food types analyzed. Total PAH concentrations were 2-7 ug/kg in the poultry, pork and beef products, and 6-28 ug/kg in the cheeses. Total (6 target) carcinogenic PAH concentrations were 0.2-3.4 ug/kg. Sausages and frankfurters were found to have lower PAH concentrations, with total (of 12 target) PAH at concentrations of 2.4-3.5 ug/kg and total (6 target) carcinogenic PAH at concentrations of <0.1-0.7 ug/kg.

5. Fresh Lake Ontario fish (edible portion) were found to contain 2.1-7.9 ug/kg total (of 11 target) PAH. Concentrations of (5 target) carcinogenic PAH ranged from 0.3-4 ug/kg, with concentrations in excess of 0.5 ug/kg found only in smelt and eel.

Another source of data for PAH concentrations in Ontario fish is the Ministry of Environment's program to monitor Great Lakes Sport Fish (Zenon Environmental Inc., 1985). The results from this program have demonstrated the presence of PAH in numerous species in all monitored lakes. For example, total (of 10 target) PAH concentrations in Lake Ontario fish ranged from 2.2-240 ug/kg, and were found in lake trout (1 of 4 samples), bass (1 of 1 sample), brown bullheads, red horse and white suckers (all samples). However, these analyses have been done on whole fish, rather than on the basis of edible portion. Therefore, their usefulness in evaluation of human exposure through diet is limited.

6. Smoked fish, fresh and canned, were found to contain similar levels of PAH related to the degree of smoking (Lawrence and Weber, 1984a). Lightly smoked fish, such as smoked haddock, cod, arctic char and canned sardines, had total (of 9 target) PAH in concentrations of 10-15 ug/kg; concentrations of (3 target) carcinogenic PAH ranged from 0.2-2 ug/kg. In contrast, more heavily smoked fish, such as smoked herring and digby chix, had total (of 9 target) PAH concentrations of 30-500 ug/kg, and carcinogenic PAH concentrations of 0.2-45 ug/kg. Similar results for smoked herring were found in another study (Alfheim, 1984), where total (of 8 target) PAH concentrations were approximately 200 ug/kg, and carcinogenic (6 target) PAH concentrations were approximately 15 ug/kg.

   The packing oils in the canned products had PAH approximately 5 times more concentrated than in the food itself.

7. Canned smoked mussels and oysters (imported) were found to contain total (of 13 target) PAH in concentrations of 65-203 ug/kg, and carcinogenic (6 target) PAH in concentrations of 4-50 ug/kg (Lawrence and Weber, 1984a). There was no apparent difference between mussels and oysters in PAH concentrations. In another study (Lawrence and Das, 1986) canned oysters (imported) had similarly high levels of (8 target) PAH (35-112 ug/kg), as well as carcinogenic (6 target) PAH (3-63 ug/kg).

   The packing oils had PAH approximately 7 times more concentrated than in the food itself (Lawrence and Weber, 1984a).

8. Canned lobster products (lobster spread and lobster meat) were found to contain total (of 12 target) PAH in concentrations of 8-367 ug/kg, and carcinogenic (6 target) PAH in concentrations of 2-166 ug/kg (Lawrence and Weber, 1984a). Similar variability was observed in another study (Lawrence and Das, 1986), and it has been attributed to the use of lobster hepato-pancreas in some products. This digestive organ has been found to selectively accumulate PAH by about 10 times compared to tail meat (Dunn et al., 1979; Dunn & Fee, 1979). Elevated PAH may be attributable to creosote contamination during impoundment or to an industrial source of marine contamination (Uthe, 1986; Williams et al., 1985).

9. Frozen and canned shrimp were found to contain generally lower levels (of 8 target) PAH - less than 1 ug/kg, except for one sample of canned shrimp, which contained 8.6 ug/kg (Lawrence and Das, 1986). In this same sample, carcinogenic PAH (B[a]A, B[a]P and B[b]F) constituted 86% of the total PAH. There was no discussion as to the reason for the variability.

10. Milled wheat fractions from wheat grain in southern Ontario were observed to contain total (of 6) PAH concentrations of 5-12 ug/kg in flour (Lawrence and Weber, 1984b). Benzo[a]anthracene and benzo[a]pyrene constituted approximately 5% and 1% respectively of the totals. PAH concentrations in the bran fraction were about 5-10 times higher than in other milled fractions, suggesting contamination was concentrated on the outer portions of the grains.

11. Breakfast cereals included wheat, corn, oats, rice and bran cereals (Lawrence and Weber, 1984b; Lawrence and Das, 1986). Total (of 11 target) PAH concentrations observed in the earlier work (Lawrence and Weber, 1984b) ranged from 6-60 ug/kg. Carcinogenic PAH (of 5 target) concentrations ranged from 0.3-13.3 ug/kg. Concentrations of both total and carcinogenic PAH were higher in wheat products, and substantially higher in wheat bran cereal than other cereals examined. In the more recent work (Lawrence, 1986), results were lower (total of 8 PAH 0.7-3.4 ug/g, carcinogenic PAH (6 target) 0.02-0.28 ug/kg).

12. Dried dairy products, such as powdered milk, were found to have total (of 8 target) PAH concentrations of approximately 1 ug/kg and carcinogenic (of 6 target) PAH constituting 3% (Lawrence and Das, 1986). Similar samples analyzed earlier (Lawrence and Weber, 1984b) were found to vary from below detection limits for all 13 target PAH to total PAH of 8 ug/kg and total carcinogenic (of 6 target) PAH of 2.7 ug/g. The variability was attributed to the drying process used.

13. Cooking oils were observed to contain total (of 14 target) PAH concentrations of 0.6-14 ug/kg and carcinogenic (of 6 target) PAH

concentrations of 0.1-4.5 ug/kg (Lawrence and Weber, 1984b). These results are similar to more extensive PAH characterizations done on margarines, butter and vegetable oils elsewhere (Hopia et al., 1986). It has been noted that PAH concentrations in vegetable oils are reduced in the oil refining processes, probably due to the steam deodorizing or filtering through activated charcoal (Larsson et al., 1987).

14. Tea leaves commonly used in Canada were observed to contain high residues of benzo[a]anthracene (7.7-11.3 ug/kg) and benzo[a]pyrene (3.3-4.2 ug/kg) (Lawrence and Weber, 1984b). However, PAH concentrations in tea infusion are about 1% those of tea leaves (Vaessen et al., 1984).

There are no Canadian data currently available on PAH concentrations in coffee or other foodstuffs. However, one review (IARC Vol. 32) has cited concentrations of B[a]A, B[a]P and chrysene in roasted coffee as being approximately 0.5-25 ug/kg each. PAH concentrations in coffee infusion are not given, but can be expected to be much lower.

7.1.2 Total Diet Studies

A total diet study is currently underway in the Food and Drug Directorate of Health and Welfare Canada (Koniker, pers. comm.). For the study, average intakes of various food types were estimated from the Nutrition Canada Survey (Health & Welfare Canada, undated, ca. 1977) and from food purchase data (Stats Can, 1982; Family Food Expenditure in Canada). Foods were purchased locally in Ottawa, were cooked "normally" (i.e., generally roasted, steamed or fried), were composited and analyzed. Preliminary results are similar to what might be expected from earlier analyses (Lawrence and Weber, 1984a, b; Lawrence and Das, 1986) of food types (Lawrence, J.F., pers. comm.), but no specific data are available.

7.1.3 Summary - PAH in Food Available in Ontario

Observed concentrations of total PAH in foods available in Ontario are presented in Table 7-1. Results show a large variability in PAH concentrations among samples of similar foods, as a result of:

- geographic location of foodstuff origin;
- method of foodstuff processing;
- method of foodstuff cooking; or
- personal food consumption pattern.

Although total diet studies will improve the accuracy of estimating the average person's exposure to PAH, the potential for large variability in actual intake is still great, with only moderate variations in dietary preferences.

7.2 PAH in Ontario Drinking Water

Drinking water supplies of five eastern Ontario municipalities and sixteen Great Lakes municipalities have been analyzed for various PAH by the Environmental Health Directorate of Health and Welfare Canada over the last ten years (Benoit et al., 1979; Williams et al., 1982; LeBel et al., 1987). Drinking water was sampled using XAD-2 resin sampling cartridges to extract and concentrate organics. Adsorbed organics were eluted with acetone/hexane and the eluates concentrated.

TABLE 7-1

Summary of PAH Levels in Foods Available in Ontario

Food	PAH Concentration (ug/kg)
Fruits & Vegetables	0.1 - 1
Fresh fish, shrimp, meat (not charbroiled or barbecued), flour and dried milk	1 - 10
Oils & Fats	1 - 30
Smoked fish, oyster, lobstres, lobsters and charbroiled meats	10 - 500

The concentrated eluates were analyzed by gas chromatography - mass spectroscopy, with compound identification using a mass spectra library.

The (9) compounds monitored were selected on the basis of their prominence in earlier analyses of Ottawa tap water, and included fluorene phenanthrene, anthracene, fluoranthene, pyrene (all locations), acenaphthalene, o-methyl-phenanthrene, benz[a]anthracene and chrysene (eastern Ontario locations) and methylanthracene (Great Lakes locations).

Concentrations of individual PAH were generally in the range of 0.1-5 ng/L, with occasional excursions (for example, Sault Ste. Marie - phenanthrene/ anthracene in summer sample 571 ng/L, in winter sample 1269 ng/L, other PAH were also elevated although not to the same extent, for example, St. Catharines winter sample, 4 PAH which ranged from 25-80 ng/L).

7.2.1 Summary

Exposure to potentially hazardous PAH may occur through ingestion of Ontario drinking water. Substantial fluctuations in concentrations of individual PAH at a single location have been demonstrated.

Concentrations of individual PAH (of 9 selected for monitoring) were generally observed in the ppt range.

7.3 PAH in Pharmaceuticals, Cosmetics

7.3.1 Coal Tars

Coal tar has been in the British Pharmacopoeia since 1893, and is in three grades. It is also available in the U.S. Pharmacopoeia (USP) (IARC No. 35). Analyses of pharmaceutical grade coal tars conducted 25 years ago (IARC No. 35 and/or Lijinsky et al., 1963) demonstrated the presence of 15 PAH in concentrations ranging from 0.23-17.5g/kg, several of which are known carcinogens, cocarcinogens, or tumor initiators. These coal tar ointments have been used for many years for the treatment of various dermatoses. One study has shown evidence of absorption through healthy adult skin after application of these ointments (Steinegger, 1984). After repeated application of 2% coal tar product (containing 12 PAH in concentrations of 40-650 ug/mL) blood levels of acetnaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene after coal tar product application were elevated from less than .04 to 11 ng/mL; 6 other PAH found in the ointment were not found in the blood samples. There was no apparent correlation between quantity of coal tar product used and PAH absorbed, although the small number of study participants and the uncontrolled application and exposure procedure may have been confounding factors. It has been noted that abraded or diseased skin may result in increased percutaneous absorption. It has also been noted that the use of a coal tar containing shampoo resulted in induction and/or enhancement of the enzyme activity considered critical to cancer induction (Merk et al., 1987). However, there are few other data characterizing exposure - absorption potential.

7.3.2 Soft and Liquid Paraffins, Mineral Oils

White soft paraffins and liquid paraffins from petroleum are widely used for external medicine and cosmetic purposes, as ointment bases for suntan oils, creams, baby toiletries, and others. Analyses of several (2) paraffin samples of each type demonstrated considerable variability in the number and concentrations of single PAH, even in the same type of product (Monarca and Fagioli, 1981). For example, the total (of 7) PAH was 6.1-82.6 ng/g (white soft paraffin) and 30.1-30.5 ng/g (liquid paraffin); carcinogenic PAH (2) concentrations were 0.1-11.6 ng/g (white soft paraffin) and 3.1-10.6 ng/g (liquid paraffin). All samples contained B[a]P.

Analyses of four commercial samples of suntan oils (available in Italy), based on mineral or vegetable oils, showed that concentrations of total (5) PAH ranged from 89-189 ng/g, and concentrations of B[a]P (found in all samples) ranged from 1.5-45.7 ng/g (Monarca et al., 1982). Anthanthrene (1.2 ng/g) was observed in the one sample based on mixed vegetable oils, which was also the sample with the highest B[a]P and total PAH concentrations. Other carcinogenic PAH, such as B[a]A, chrysene, were not detected.

7.3.3 Summary

Exposures to potentially hazardous PAH may occur through the use of pharmaceuticals based on coal tar, and personal care products such as suntan oils and presumably other cosmetics with similar bases. Coal tar pharmaceuticals have PAH concentrations in the ppm range as well as medicinal paraffins. Use of these products may have effects both directly on skin and systemically (through absorption).

7.4 PAH in Indoor Air

Sources of PAH in indoor air include:

- outside (ambient) air, infiltrating the building envelope;
- combustion processes (such as wood stoves and kerosene heaters); and
- tobacco smoke.

7.4.1 Effects of Combustion Processes (for Heating)

It is clear that wood smoke particulate matter contains PAH, and that the emission of PAH type and amount during wood burning depends upon the kind of wood burned, the moisture content and the burning regime. PAH emission factors have been determined for fireplaces, baffled and non-baffled stoves burning two different wood types (Peters et al., 1981; Travis et al., 1985). However, these data were determined by measuring flue gas constituents; they are therefore not indicative of PAH concentrations inside houses were wood is burned.

The effects of the use of wood burning stoves on indoor-outdoor PAH concentrations have been carried out in Whitehorse by the Monitoring and Criteria Division, Environmental Health Directorate, Health and Welfare Canada (R. Otson, pers. comm.). Analyses were done for over 100 aromatic compounds, including many PAH. As many homes in the Whitehorse area are heated by wood, the study is expected to demonstrate the effects of the use of wood stoves on indoor air quality. Preliminary results indicate that PAH were largely seen in indoor air samples (detection limits estimated to be approximately 5 ng/m^3 for higher molecular weight PAH approximately 3 ng/m^3 for lower molecular weight PAH). PAH concentrations indoors were also generally lower than those outdoors, indicating that neither outdoor air nor backdrafting from the wood stoves was contributing significantly to long-term average indoor PAH concentrations.

An American study of 24 homes in Vermont (Sexton et al., 1984) also demonstrated that outdoor concentrations of PAH frequently exceed those in homes with wood stoves. Total (of 8 target) PAH indoors ranged from 1.3-20.4 ng/m^3, those outdoors ranged from 3.0-35.3 ng/m^3. Total (of 5) carcinogenic PAH indoors ranged from 0.9-15.3 ng/m^3.

A Norwegian study (Alfheim, 1984) demonstrated that burning wood in an "airtight" stove caused small increases in indoor total PAH concentrations. Total (of 30 target) PAH indoors ranged from <1 ng/m^3 in an electrically heated house to 16 ng/m^3 in one with a wood stove operating normally. However, when wood was burned in an open fireplace, indoor PAH concentrations increased substantially to 150-206 ng/m^3 (B[a]P concentrations 13-18 ng/m^3).

PAH are also emitted during kerosene combustion, 18 PAH have been identified in kerosene soot (Kaden et al., 1979). Portable kerosene space heaters which are common in the U.S. were studied recently, in well-tuned and badly-tuned operating conditions (Traynor et al., 1986). Phenanthrene and fluoranthene were observed in all tests, with source strengths of 1.9-16 ug/h (phenanthrene) and 0.1-1.8 ug/h (fluoranthene). Anthracene, chrysene, and indeno[1,2,3,-cd]pyrene were also observed in individual tests, with source strengths of 2.27, 0.05 and 0.12 ug/h respectively. Another study demonstrated the presence of benzo[a]-pyrene, benzo[b]fluoranthene, and benzo[k]fluoranthene in kerosene heater emission particulate matter (Tokiwa et al., 1985). However, there was not enough information given to determine PAH emission rates. There were no data on PAH concentrations in air resulting from the use of kerosene space heaters.

7.4.2 Effects of Tobacco Smoke

An eight home pilot study of indoor-outdoor concentrations of PAH and PAH derivatives was also carried out recently by the U.S. EPA (Wilson and Chuang, 1987). Its objective was to compare concentrations in homes with and without smokers. Preliminary results indicate indoor concentrations of PAH (14 target compounds of interest) in homes without smokers were generally slightly higher than outdoor concentrations (although the differences may not have been analytically or statistically significant), and that all target compounds had higher concentrations in homes with smokers. For example, concentrations of individual PAH for a non-smoking house were 0.18-29 ng/m^3 (outdoors), 0.18-59 ng/m^3 (indoors), total (of 14) PAH 81-97 ng/m^3; for the smoking house, they were 0.34-54 ng/m^3 (outdoors), 0.64-210 ng/m^3 (indoors), total (of 14) PAH 121-245 ng/m^3.

Concentrations of (13 target) PAH were monitored in a 36 m^3 room with a single air change per hour, under conditions of no smoking and smoking approximately 40 cigarettes over an 8-hour period (IARC No. 29). Total PAH in non-smoking conditions was 134 ng/m^3, in smoking conditions averaged 429 ng/m^3. Concentrations of individual PAH ranged from <2-50 ng/m^3 (no smoking) and from <2-116 ng/m^3 (smoking); concentrations of B[a]P increased with smoking from <3 ng/m^3 to 22 ng/m^3.

Concentrations of (6 target) PAH were also monitored in a 38 m^3 closed room with natural ventilation, under no smoking and smoking 15-30 cigarettes (Grimmier et al., 1977). Total PAH in non-smoking conditions was 32 ng/m^3, in smoking conditions averaged 214 ng/m^3. Concentrations of individual PAH ranged from < 1-75 ng/m^3 (no smoking) and from 27-214 ng/m^3 (smoking); concentrations of B[a]P increased with smoking from 5 ng/m^3 to 88 ng/m^3.

Numerous (38) analytical studies have shown the presence of 37 PAH in tobacco smoke, and quantitative data on their occurrence in cigarette mainstream and sidestream smoke, cigar and pipe smoke are summarized in one review (IARC Monograph #38, 1983). For example, mainstream cigarette smoke contains the following amounts of carcinogenic PAH:

	ug/100 cigarettes
Benz[a]anthracene	0.4-7.6
Benzo[b]fluoranthene	0.4-2.2
Benzo[f]fluoranthene	0.6-2.1
Benzo[c]phenanthrene	present
Benzo[a]pyrene	0.5-7.8
Chrysene	0.6-9.6
Dibenz [a,c]anthracene	present
Dibenz [a,h]anthracene	0.4
Dibenz [a,j]anthracene	1.1
Dibenzo[a,e]pyrene	present
Dibenzo[a,h]pyrene	0.17-0.32
Dibenzo[a,i]pyrene	0.4-2.0
Indeno[1,2,3-cd]pyrene	

Constituents in sidestream smoke may vary somewhat in relative proportion to those in mainstream smoke, but are present to the same order of magnitude.

Total PAH in mainstream cigarette smoke range from 0.31-2.1 ug/cigarette (sum of individual PAH concentrations found by different authors, generally using non-filter cigarettes smoked under standardized lab conditions). It should be noted that most of the data are based upon smoking patterns of 30 years ago, which are not the same today. Conventional filter types can be expected to reduce compounds found in the particulate phase (such as PAH); however, reduced nicotine delivery induces the smoker to puff more frequently and inhale more deeply; also, by obstructing the holes in perforated filter tips, the smoker can inhale more smoke than would be expected. Therefore, the above data may be subject to greater variability than indicated by the ranges given.

7.4.3 Indoor PAH from Miscellaneous Sources

PAH result from the combustion or pyrolysis of carbonaceous matter. Therefore, one potential domestic source for PAH is pyrolysis during cooking. No studies were found concerning PAH concentrations in air during certain domestic high temperature cooking processes (e.g., deep fat frying). However, the studies of airborne PAH in homes cited earlier (Otson, pers. comm.; Wilson & Chuang, 1987) involved long-term monitoring in several locations (including kitchens), and no cooking effects were noted.

Emissions arising from pyrolysis of insecticidal coils have been found to contain 30 PAH in the air-entrained particulate, at concentrations of 500-

700 ng per mg particulate (Lazaridis, 1987). Carcinogenic PAH (benzo[a]pyrene, benz[a]anthracene, chrysene, and indeno (1,2,3-cd) pyrene were in concentrations of 131-169 ng/mg. Assuming a hypothetical use of one coil in a 250 m^3 summer house with 3 air changes per hour, good mixing, and a 10 hour burning time, total PAH concentration is estimated to be 15 ng/m^3.

7.4.4 Summary

Indoor PAH concentrations are generally less than, and sometimes similar to those in ambient air, for homes without combustion devices and smokers. The use of air-tight wood burning appliances generally increases indoor PAH concentrations only slightly or not at all; the use of open fireplaces increases total PAH concentrations substantially, concentrations of 200 ng/m^3 having been observed. The use of kerosene space heaters is expected to elevate total PAH concentrations, but the effect has not been characterized. Tobacco smoking in the home increases PAH concentrations substantially - total (of 14) PAH concentrations of 121-245 ng/m^3 have been observed in homes. Tobacco smoking appears to be the most significant single source of PAH exposure, with the mainstream smoke of one cigarette estimated to contain 0.31-2.1 ug total PAH and 0.05-0.33 ug carcinogenic PAH.

7.5 Estimated Levels of Human Exposures

The major routes of exposures to PAH appear to be ingestion of food, inhalation of tobacco smoke, inhalation of ambient air, and ingestion of drinking water. Average exposures can be estimated, based upon observed PAH concentrations in the various media and on average rates of ingestion/inhalation.

A summary of estimated average exposures has been compiled in Table 7-2, based upon data given in the previous sections. The assumptions made in deriving the estimate are also in the table. The purpose of the estimate is to illustrate the relative importance of exposure routes/consumption patterns in PAH exposures.

There are several weaknesses in this estimation process. The data for "total PAH" and "carcinogenic PAH" are not entirely comparable, as different studies selected different target PAH. Therefore, reported levels may be biased low, because they do not include PAH not looked for. Similarly, most authors' results have not been corrected for analytical recovery rates, which vary substantially with individual PAH, but may average 60-90%.

TABLE 7-2

Estimated Average PAH Exposures per Individual in Ontario

		Total PAH		Carcinogenic PAH	
	Estimated Intake[1] kg/yr	Mid-Range Conc. ug/kg	Intake ug/yr	Mid-Range Conc. ug/kg	Intake ug/yr
1. Ingestion of Food					
Fresh fruits	50	——————no data——————			
Vegetables	88	0.3	261	0.3	26
Meat, fresh & canned, beef, pork	40[2]	1.3	52	0.3	52
Chicken and other	7[3]	18	126	10	70
Meat, cured/prep'd	15	5	75	1.6	24
Fish, fresh, fry, canned	4.2	38	16	0.4	2
Fish, cured	0.1	10	1	1.0	0.1
Shellfish[4]	0.4	172	69	23	9
Cheese	6.0	11	7	1.6	10
Oils, fats	8.0	6.7	54	2.2	18
Cereals, Grains[5]	5.6	2.0	11	0.1	0.6
Rice	2.9		no data		
Flour and mixes	8.2	8.5	70	0.5	4
Baked goods, pasta[6]	93	8.5	791	0.5	47
Milk, dried	0.3	3.5	1	1.4	0.4
Milk, fresh fluid	93L		no data		
Total Food			1299 (ug/yr)		263 (ug/yr)
2. Ingestion of Drinking Water					
	2 L/day	750 ng/L	36.5	2.1[7] ng/L[7]	1.5 ug/yr
3. Inhalation					
5000 m^3/y (WHO) (ng/m^3)					
Ambient (0.3)		20	30	22	3
Indoor (0.7)					
- non-smoking		20	70	2	7
- smoking/fireplaces		200	700	20	70
Total Air			100-730 ug/yr		10-73 ug/yr
TOTAL			1.5-2.1 mg/yr		0.45-09.51 mg/yr
Smoker	10 cig/day	0.9 ug/cig	3.3 mg/yr	0.14 ug/cig	0.51 mg/yr

Footnotes:

[1] Intakes estimated from reference (Statistics Canada - Family Food Expenditure in Canada 1982, Table 13, based on 2.74 persons per Ontario family reported in Table 1).

[2] Assumed fried, steamed, roasted conventionally.

[3] Assumed charbroiled/barbecued.

[4] Assumed [PAH] of canned, smoked oysters.

[5] Assumed [PAH] from more recent data.

[6] Assumed [PAH] of flour.

[7] No Canadian data. Assumed U.S. average (Santodonato et al., 1981).

Perhaps the major weakness in the estimation process is the large variabilty in the observed PAH concentrations in foods, even similar food types sampled and analyzed at the same time. However, with this in mind, the estimates do suggest the following:

1. That mainstream tobacco smoke is the single largest source of PAH and carcinogenic PAH exposure.
2. That sidestream tobacco smoke is a significant contributor to total PAH exposures of non-smokers.
3. That for non-smokers, ingestion of food constitutes the major exposure pathway.
4. That a moderate change in food consumption patterns can result in a significant variation in PAH intake.

8.0 ASSESSMENT OF ENTRY, MOBILITY AND FATE OF POLYCYCLIC AROMATIC HYDROCARBONS

This section attempts to integrate and interpret the data presented in the previous sections by means of rudimentary modelling results and evaluation of modifying factors which may be important in estimating a PAH budget for Ontario.

Several important aspects are discussed.

- Implications of physical partitioning of PAH into environmental media.
- Implications of chemical transformations (differing for vapours and particles).
- Estimates of total and speciated PAH emissions in Ontario.
- Evaluative models for PAHs and PAH mixtures, as they relate to estimation of exposure pathways.
- Source - receptor relationships, especially for mixtures.

8.1 Physical Partitioning and Chemical Transformation of PAH and PAH Mixtures

It is important to determine whether PAH mixtures can be traced from source to receptor, more to the point, from multiple sources to a receptor through multiple pathways (source apportionment). The potential for determining characteristic source profiles to be used in source apportionment has been discussed in Chapter 4. The relative concentrations of PAH in a mixture emitted or discharged from a source begin to change upon entering the environment, by both physical and chemical processes. This section describes how these processes influence the "traceability" of PAH from source to receptor.

The vapour- and particulate-phase components of emissions to the atmosphere will partition differently. Coarse particles will deposit near the source. Particles smaller than about 20 um aerodynamic diameter, which are dispersed in the atmosphere and behave as passively transported contaminants, will behave differently from vapours or gases, primarily because of their greater susceptibility to precipitation removal (rainout or washout). PAH vapours are hydrophobic (see Table 2-2), so that their removal in rain or snow will be minimal, and their lifetimes in the atmosphere are very likely to be somewhat longer than those for PAH predominantly bound to particles, at least with respect to physical processes.

Vapour-particle partitioning of PAH will change as a contaminated air mass disperses, since the fraction of a given PAH that is bound to particles depends not only upon its vapour pressure (or related sorptive properties) but also upon the absolute particle concentration (Cupitt, 1980; Yamasaki et al., 1982; Mackay et al., 1986). Thus, PAH will be partitioned more toward the vapour-phase in conditions of lower particle concentration, such as in rural areas away from sources.

Chemical transformation of vapour-phase PAH and particle-bound PAH differ (Korfmacher et al., 1980). Vapour-phase chemical reactions will depend, of course, on the presence of co-pollutants in the air mass into which the PAH are emitted and the intensity of solar actinic (i.e., photochemically active) radiation. The rate of nitration of pyrene, for example, depends upon the available concentrations of oxidant, nitrogen oxides and water vapour. See Chapter 5 and a review of the mechanism by Finlayson-Pitts and Pitts (1986). Furthermore, atmospheric reactions, nitration, for example, do not stop with the formation of the initial reaction product. Nitro-PAH have been shown to photolyse readily to produce keto-derivatives (quinones). That is, each reaction is one step toward complete oxidation of the hydrocarbon. Oxidation eventually leads to cleavage of aromatic rings to form aldehydes and acids. See Finlayson-Pitts and Pitts (1986, p.935) and the discussion in Chapter 5 on the analogous aquatic and terrestrial fate data.

The foregoing implies that, at any time after release of emitted PAH mixtures, both physical and chemical separation processes will have changed the composition and properties of the mixture. A possible exception to this may be emissions into a very cold, dry, and otherwise unpolluted air mass experiencing low levels of solar actinic radiation. Under the latter circumstances, which may obtain during a portion of Ontario's winter, airborne mixtures may be transported significant distances with relatively little modification, except for settling of larger particles. Evidence for this hypothesis is lacking, but the relatively slow transformation rates of PAH in LRT from Europe to Scandanavia observed by Nielsen et al. (1983) indicate that under certain atmospheric conditions, little transformation may take place.

Thus, at a receptor site, the composition and characteristics of the contributions of various sources to total PAH burden will be intermediate between their initial characteristics and their ultimate state. The degree of modification depends on the time between emission and reception.

Near emission sources, the particle-phase PAH will have changed composition least and will likely be a relatively stable indicator of source origin. Away from dominant emission sources, where both direct source-receptor and indirect pathways (influenced by multi-media partitioning and transformation) contribute significantly, source information in the chemical composition of the PAH fraction may be unresolvably masked. Source information is also confused by mixing with emissions from multiple sources.

The foregoing suggests that the only reliable indicator within the PAH fraction of PAH burden in the atmosphere is that set of PAH which predominates in the particulate phase. Simple fugacity modelling to demonstrate which of the priority PAH behave in that manner is described in the next section. This argument also suggests that constituents other than PAH of media through which exposure may occur, such as chemical elements or stable compounds, ought to be considered in assessing PAH source contributions to exposure.

Nielsen (1984) has described a reactivity classification system for PAH (Section 5.1.1), which includes explicitly 25 different PAH. Only those PAH which are at least as stable as, for example, the benzopyrenes (Nielsen's Classes II and III) are likely to be useful to characterize PAH mixtures for source apportionment purposes.

8.2 Modelling the Fate of PAH Compounds

The fate of polycyclic aromatic compounds is dependent on their physical, chemical and biological properties, as well as the environmental conditions such as temperature, transport parameters and biological activity. It is possible to model this fate at various levels of sophistication and accuracy dependent on the availability and reliability of data. Mackay et al. in a series of papers have presented a structured format for performing these fate assessments at various levels of sophistication. This work will apply the "fugacity" models of Mackay to the extent that is justified by the available data.

As an introduction to the application of fugacity models, it is appropriate to provide a brief review of the concepts. Mackay and Paterson (1982) have described four levels of environmental transport and fate model calculations based on the fugacity approach (Level I to Level IV). Fugacity is a thermodynamic quantity related to chemical potential (or activity), which characterizes the escaping tendency (viz., the Latin root of fugacity) of a chemical from one phase to another. By appropriately defining environmental compartments and their components as confined phases, the model calculations may be used to characterize the movement, depletion and accumulation of chemicals among such compartments.

The Level I fugacity model treats the apportionment of a chemical among environmental compartments at equilibrium steady state, without mass transfer flow between compartments. Levels II, III and IV treat progressively more complex situations, culminating in the simulation of a nonequilibrium, nonsteady-state flow system at Level IV. The latter model is necessasry to simulate the behavior of the real environment, which has time-dependent emissions and discharges. The choice of any of the fugacity models depends on the amount and quality of data available for a given chemical.

The principal objective of this section is to characterize the tendencies of the priority PAH to move into the various environmental media compartments. A Level I model suffices for this purpose. In a later section, an example Level III (non-equilibrium, steady-state, with flow) calculation for B[a]P is presented.

Additional information about this approach to modelling environmental behavior of chemicals may be found in Cohen (1986); Ryan and Cohen (1986); Mackay, Joy and Paterson (1983); Mackay, Paterson and Schroeder (1986); IJC (1987, 1988) and Cohen and Ryan (1985).

The next section describes the Level I calculations for the priority PAH, with the objective of evaluating their potential for partitioning into and accumulating in selected environmental compartments.

Level One

This is the simplest of the models and easiest to apply. The necessary compound data are molecular weight, water solubility, vapour pressure and octanol-water partition coefficient. The compound is then distributed in the environment based on these properties and the assumption that equilibrium has been achieved. The assumption of equilibrium holds for real partitioning processes in the absence of competing processes, given enough time. The equilibrium partitioning indicates the tendency of a chemical to accumulate in any of the media or phases included. This distribition may represent the steady-state distribution in more complex (i.e. realistic) situations. In a later section, the results of the simple calculations are compared with more realistic model results to indicate the level of confidence which can be placed in the Level I model.

It is not necessary at this level to know the emission rate of the compound because equilibrium is assumed and because no statements will be made with respect to the life expectancy of the compound. The result of this level is simply the distribution of the compound expected in a typical environment and at equilibrium. The volumes of the various environmental segments are given in Table 8-1. These values were chosen to be representative of Southern Ontario. As can be seen, the environment is divided into six compartments (air, water, soil, sediment, suspended sediment and biota). A number of other assumptions are included in this application of the model. The partitioning between solid and water is described by a partition coefficient, Kp, which can be obtained from the organic carbon-water partition coefficient, Koc, using the fraction organic carbon in the soil (foc).

$$K_p = f_{oc} K_{oc}$$

The soil is assumed to have a fraction organic carbon of 2%. The value of organic carbon-water partition coefficient can be obtained from the octanol-water partition coefficient by the use of the following correlation:

$$K_{oc} = 0.41\ K_{ow}$$

A similar process is used for the sediment and the suspended sediment, except the fraction organic carbon is 4%. For biota, the partitioning is handled by a bioconcentration factor which can be obtained from the octanol-water partition coefficient using the following correlation:

$$BCF = 0.048\ K_{ow}$$

"Air" refers only to the vapour phase in this model. Later on, in Section 8-4, a model including airborne particles is described. In any case, the small mass and short lifetime of airborne particles mean that the capacity of this sub-compartment is very small compared with others.

TABLE 8-1

Volumes of Environmental Segments

Fugacity - Level 1

UNIT WORLD INFORMATION

	Volume (m^3)	Foc*	Density (g/m^3)
Air	6.0E+09		1
Water	7000000		1000
Soil	45000	0.02	1500
Sediment	21000	0.04	1500
Suspended Sediment	35	0.04	1500
Biota	7		1000
Temperature (°C)	20		

* Fraction Organic Carbon

8.3 Results and Discussion

The property data for the various PAHs have been presented elsewhere in this report (see Table 2-2). Although only a small amount of property data is necessary to perform the "level one fugacity model", the data are unavailable for a number of the PAH in this study. Shown in Table 8-2 are the level one results for 22 of the 47 PAH in the study. Of the remaining 25 compounds, 20 are not included because the vapour pressure had not been measured nor estimated. The remaining 5 were not included because more than one of the required data was unavailable.

In Table 8-2 the mole percentage distribution is given for each of the PAH, as well as the property data that were used to perform the calculation. The 4 compartments: soil, sediment, suspended sediment and biota are combined into a compartment called 'organic'. The justification for this is that four compartments are all represented by the affinity of the compound for the organic phase.

To assist in the interpretation of these results, Table 8-3 has been prepared to illustrate the distribution of the compounds. Table 8-3 is a matrix grouping the compounds of similar distribution together. The classes are dominant, significant, slight and trace for each compartment. Pyrene results show that the air, water and organic distribution is 1.8, 5.6 and 92%, respectively. Thus, pyrene can be found in the dominant category for the organic phase, slight category for the water phase and slight category for the air phase.

TABLE 8-2

Results for Level One Analysis of PAH Data

Compound	MWt (g/mol)	Vapour Pressure (Pa)	Aq. Sol. (g/m³)	LOG K_{ow}	Distribution - Mole Percent						
					Air	Water	Organic	Soil	Sed.	Susp. Sed.	Biota
ACE	154.21	1.3E+00	4.33	4.03	86	5.3	8.7	4.5	4.2	0.007	0.003
ACEY	152.21	8.9E-01	8	4.57	47	7.9	45	23	22	0.04	0.01
ACR	179.23	1.3E+02	100	3.40	98	1.2	0.45	0.23	0.22	0.0004	0.0001
A	178.24	4.9E-04	0.053	4.45	9.8	17	73	38	35	0.06	0.02
B[a]A	228.30	2.6E-08	0.65	5.91	3.0E-06	0.8	99	51	48	0.08	0.03
B[a]P	252.32	7.3E-07	0.004	6.50	0.003	0.21	100	52	48	0.08	0.03
B[e]P	252.32	7.3E-07	0.0054	5.96	0.009	0.71	99	51	48	0.08	0.03
B[ghi]PER	276.34	8.8E-09	0.00045	6.94	0.0001	0.08	100	52	48	0.08	0.03
B[k]F	252.32	1.3E-07	0.000757	6.84	0.001	0.09	100	52	48	0.08	0.03
CARB	167.21	1.2E-03	93	3.29	0.06	77	23	11.9	11.1	0.02	0.01
CHR	228.30	4.7E-09	0.0022	5.91	0.0001	0.8	99	51	48	0.08	0.03
COR	300.36	2.0E-10	0.0146	8.00	9.0E-09	0.007	100	52	48	0.08	0.03
DB[ac]A	278.40	1.8E-12	0.0005	7.01	2.0E-08	0.064	100	52	48	0.08	0.03
DB[ah]A	278.36	1.8E-12	0.0005	7.01	2.0E-08	0.064	100	16	15	0.02	0.01
F	202.30	1.8E+00	0.26	5.26	94	0.19	5.3	2.8	2.6	0.004	0.002
FLN	166.20	9.3E-02	1.69	4.18	49	15	35	18	17	0.03	0.01
INP	276.34	1.9E-12	0.22	6.64	1.0E-10	0.15	100	52	48	0.08	0.03
MPHEN	192.26	2.3E-11	0.269	5.17	2.0E-08	4.2	96	50	46	0.08	0.03
PHEN	178.24	4.8E-02	1.277	4.46	30	13	57	29	27	0.05	0.02
P	202.26	7.0E-04	0.16	5.03	1.8	5.6	92	48	45	0.07	0.03
QUINOL	129.17	1.3E+02	60000	2.03	9	90	1.5	0.76	0.71	0.001	0.0005
TRI	228.30	5.0E+3	0.038	5.21	100	9.0E-06	0.0002	0.0001	0.0001	2.0E-07	7.0E-08

Legend:

MWt = molecular weight (g/mol)
Pa = Pascals
Aq. Sol. = Aqueous Solubility (g/m³)
Log K_{ow} = logarithm (base 10) of the octanol-water partition coefficient

"Organic Phase" is apportioned into its four compartments in proportion to the mass of organic carbon in each. See Table 8-1.

TABLE 8-3

Distribution of PAH into Air, Water and Organic Components Based on Raw Property Data

	AIR	WATER	ORGANIC*
Dominant (>50 mol%)	ACE ACR F TRI	QUINOL CARB	A B[A]A B[A]P B[E]P B[GHI]PER B[K]F CHR COR DB[AC]A INP MPHEN PHEN P DB[AH]A
Significant (<50 mol% >10 mol%)	ACEY FLN PHEN	A FLN PHEN	ACEY FLN CARB
Slight (<10 mol% >0.1 mol%)	A P QUINOL	ACE ACEY ACR B[A]A B[A]P B[E]P CHR F INP MPHEN P	ACE ACR F QUINOL
Trace (<0.1 mol%	B[A]A B[A]P B[E]P B[GHI]PER B[K]F CHR COR DB[AC]A INP MPHEN DB[AH]A CARB	B[GHI]PER B[K]F COR DB[AC]A DB[AH]A TRI	TRI

* Includes soil, sediment, suspended sediment and biota.

See Table 2-2 text for full name of compounds.

Table is based on a Fugacity Level I calculation.

These distribution data can be of assistance in setting priorities for obtaining additional data. That is, for a compound such as triphenylene, the important reaction rates will be those in the air phase because the majority of the compound will reside in that phase. The reaction rates in the soil phase will be of secondary importance and therefore do not need to be known as accurately.

Table 8-4 is a summary of the results of a sensitivity study for each of the compounds. The table includes a range of vapour pressure, water solubility and K_{ow} values from the literature. The Level I distribution in the three phases is given for each extreme of one property holding fixed the base, or preferred, values of the properties (Table 8-2) for the other parameters. As an example, pyrene tests the sensitivity of the results to vapour pressure by using 7.0E-5 and 700 E-5 Pa in conjunction with a water solubility of 0.16 g/m^3 and log K_{ow} of 5.03.

The result of this sensitivity test is a distribution range of 0.2-15, 5.7-4.9 and 94-80 mole percent for the air, water and organic phases, respectively. A similar analysis was performed for the water solubility and K_{ow} and also on each of the compounds. The choice of the range of data to test was based on one of two criteria, whichever produced the larger range, as follows. The first is vapour pressure, a factor of 5 in each direction, water solubility, a factor of 2, and log K_{ow}, plus or minus 0.2. These are based on a subjective assessment of the data in the database. The second criterion was based on the premise that if data for a particular compound suggest a wider range is necessary, then that range was used.

TABLE 8-4

Sensitivity Analysis of Input Data
for Level One Analysis

Compound	Vapour Pressure (Pa)	Aqueous Solubility (g/m^3)	Log K_{ow}	Vapour Pressure			Aqueous Solubility			K_{ow}		
				Air	Water	Organic	Air	Water	Organic	Air	Water	Organic
ACE	0.26-6.5	2.1-8.6	3.83-4.23	55-97	17-1.2	28-2.0	93-76	2.8-9.3	4.5-15	89-82	5.5-5.0	5.7-13
ACEY	0.18-4.5	4.0-29	4.37-4.77	15-82	13-2.7	72.16	64-20	5.4-12	31-68	57-37	9.5-6.2	34-56
ACR	0.13-130	50-200	3.2-3.6	5.6-98	68-1.2	26-0.4	99-97	0.6-2.3	0.2-0.9	98-98	1.2-1.2	0.3-0.7
A	(0.98-24)E-4	0.026-0.1	4.15-4.75	2.1-35	18-12	79-52	18-5.5	15-18	66-77	16-5.7	27-9.8	58-84
B[a]A	(5.2-130)E-9	0.3-1.3	5.7-6.1	0-0	0.8-0.8	99-99	0-0	0.8-0.8	99-99	0-0	1.3-0.5	99-99
B[a]P	(1.5-37)E-7	(4-800)E-5	6.3-6.7	0-0	0.2-0.2	100-100	0.3-0	0.2-0.2	99-100	0-0	0.3-0.1	100-100
B[e]P	(1.5-37)E-7	(27-100)E-4	5.8-6.4	0-0	0.7-0.7	99-99	0-0	0.7-0.7	100-99	0-0	1-0.3	99-100
B[ghi]PER	(1.8-4400)E-10	(2.0-9.0)E-4	6.7-7.2	0-0	0.1-0.1	100-100	0-0	0.1-0.1	100-100	0-0	0.1-0	100-100
B[k]F	(1.2-65)E-8	(4.0-15.0)E-4	6.6-7.1	0-0	0.1-0.1	100-100	0-0	0.1-0.1	100-100	0-0	0.2-0.1	100-100
CARB	(2.4-60)E-4	46-200	3.1-3-5	0.01-0.3	77-77	23-23	0.1-0.03	77-77	23-23	0.1-0.1	84-67	16-33
CHR	(9.4-240) E-10	0.001-0.004	5.6-6.1	0-0	0.8-0.8	99-99	0-0	0.8-0.8	99-99	0-0	1.6-0.5	98-99
COR	(2-9800)E-13	0.0001-0.03	7.8-10	0-0	0-0	100-100	0-0	0-0	100-100	0-0	0-0	100-100
DB[ac]A	(3.6-91)E-13	0.0002-0.001	6.8-8.0	0-0	0.1-0.1	100-100	0-0	0.1-0.1	100-100	0-0	0.1-0	100-100
DB[ah]A	(3.6-91)E-13	0.0002-0.001	6.8-8.0	0-0	0.1-0.1	100-100	85-53	0-0	15-47	79-60	0-0	21-40
F	.0018-9.0	0.1-0.5	5.1-5.5	1.7-99	3.4-0	95-1.2	98-90	0.1-0.4	2.1-9.8	96-91	0.2-0.2	3.8-8.9
FLN	(9.3-93000)E-5	0.8-3.4	3.9-4.4	0.1-91	30-2.8	70-6.5	67-32	9.9-20	23-47	59-40	18-12	22-48
INP	(3.7-93)E-13	0.07-0.4	6.4-6.8	0-0	0.1-0.1	100-100	0-0	0.1-0.1	100-100	0-0	0.3-0.1	100-100
MPHEN	(4.6-114)E-12	0.07-0.5	5.0-5.4	0-0	4.2-4.2	96-96	0-0	4.2-4.2	96-96	0-0	6.1-2.5	94-97
PHEN	(4.8-480)E-3	0.4-2.5	4.3-4.7	4.2-81	18-3.4	78-15	58-18	7.7-15	34-66	37-21	16-9.1	48-69
P	(7.0-700)E-5	0.03-0.3	4.8-5.3	0.2-15	5.7-4.9	94-80	8.7-0.9	5.2-5.7	86-93	2.8-1.0	9.1-3.1	88-96
QUINOL	1.3-133	6000-120000	1.8-2.2	0.1-9.0	98-90	1.6-1.5	50-4.7	49-94	0.8-1.5	9.1-9.0	90-89	0.9-2.1
TRI	50-5000	0.006-0.08	5.0-5.4	100-100	0-0	0-0	100-100	0-0	0-0	100-100	0-0	0-0

TABLE 8-5

Distribution Changes Due to Vapour Pressure Sensitivity

	AIR		WATER		ORGANIC*	
Dominant (>50 mol%)	ACR F	acey fln phen		acr	PHEN	acey f fln
Significant (<50 mol% >10 mol%)	ACEY FLN PHEN	a p	FLN PHEN	ace acey	ACEY FLN	ace acr phen
Slight (<10 mol% >0.1 mol%)	A P	acr f fln phen carb	ACE ACEY1 ACR F	fln phen	ACE ACR F	fln
Trace (<0.1 mol%)	CARB			f		

* Includes soil, sediment, suspended sediment and biota.

See text for full name of compounds.

Capital letters refer to positions consistent with Table 8-3 while lower case letters refer to potential classification changes due to errors in the value of the vapour pressure of the compound.

TABLE 8-6

Distribution Changes Due to Water Solubility Sensitivity

	AIR		WATER		ORGANIC*	
Dominant (>50 mol%)		acey fln phen	QUINOL		PHEN	acey
Significant (<50 mol% >10 mol%)	ACEY FLN PHEN	a quinol	FLN PHEN	acey quinol	ACEY	ace phen
Slight (<10 mol% >0.1 mol%)	A QUINOL	b[a]p	ACEY	fln phen	ACE	
Trace (<0.1 mol%)	B[A]P					

* Includes soil, sediment, suspended sediment and biota.

See text for full name of compounds.

Capital letters refer to positions consistent with Table 8-3 while lower case letters refer to potential classification changes due to errors in the value of the water solubility of the compound.

TABLE 8-7

Distribution Changes Due to K_{ow} Sensitivity

	AIR		WATER		ORGANIC*	
Dominant (>50 mol%)		acey fln			PHEN	acey
Significant (<50 mol% >10 mol%)	ACEY FLN	a	ANTHRACE PHEN		ACEY	ace phen
Slight (<10 mol% >0.1 mol%)	A			a b[k]f phen	ACE	
Trace (<0.1 mol%)			B[K]F			

* Includes soil, sediment, suspended sediment and biota.

See text for full name of compounds.

Capital letters refer to positions consistent with Table 8-3 while lower case letters refer to potential classification changes due to errors in the value of the K_{ow} of the compound.

To assist in the interpretation of these sensitivity tests, Tables 8-5, 8-6 and 8-7 were prepared. In each table, the potential classification changes with respect to Table 8-3 are given.

For example, in Table 8-5, the base location of pyrene is given in the left hand column of each compartment pair. As a result of realistic changes in vapour pressure, the classification of pyrene in the air phase may move from slight to significant (right hand column). Compounds which do not change classification are not shown.

Although the classifications are subjective, some interesting conclusions can be made. It is evident that uncertainty associated with the vapour pressure of some compounds can lead to significant changes in the predicted distribution of that compound.

Combining this with the fact that vapour pressure data are unavailable for 20 compounds, it is evident that a principal weakness in PAH data is vapour pressure. The uncertainty in the water solubility and K_{ow} is of secondary importance.

Some of the results in Tables 8-2 and 8-3 may be counter-intuitive for some PAH. For example, pyrene might be expected to be found primarily in air because of its relatively high vapour pressure. The results of the sensitivity analysis shown in Table 8-4 indicate that the range of expected partitioning of pyrene may be from 0.2 to 15% into the air compartment, and that for the entire range of current values of its properties, pyrene is expected to be found predominantly associated with the "organic" compartments. It is an experimental fact that airborne pyrene does appear predominantly in the vapour phase (e.g., Dann, 1988), undoubtedly due to its moderately high vapour pressure. The Level I model is suggesting, however, that because of pyrene's high water solubility and moderately high affimity for organic carbon (K_{oc}), it will tend to end up in the long term in the "organic" compartments, like many of the heavier PAH with much lower vapour pressure.

Table 8-4 indicates the significant ranges of predictions that are possible based on available physical property data. Tables 8-5 to 8-7 reflect those ranges calculated in the sensitivity tests.

8.4 Advanced Model Predictions

The level one model results are shown in Table 8-2 and the results of sensitivity tests are shown in Table 8-4. The distribution data should be used to decide on priorities for the obtaining of secondary property data. Vapour pressure data uncertainty and unavailability is the greatest shortcoming of the available PAH database.

As described by the model of Mackay et al. (1986), certain PAH may cycle many times between aqueous and atmospheric media before reaching their ultimate residence. Based on the foregoing analyses, the ultimate media will be sediments and soils for most PAH. Recognizing that atmospheric transformation processes are oxidative, it is probable that sequential oxidative steps will make the PAH less hydrophobic (phenolic and acidic moieties being added) and with decreasing vapour pressures, so that the probability of incorporation into surface soil or suspended sediment and then bottom sediment increases.

Until reaching buried sediments or sub-surface soils, where anaerobic (reductive) chemical and microbiological processes dominate, it must be recognized that PAH are not as persistent as many of the environmentally longer-lived organic compounds, such as the organochlorine pesticides and related substances. See Chapter 5. This means that one should attempt to characterize PAH mixtures only by their most stable, particle-bound components. These components include, of course, non-PAH compounds, and in particular, elements and inorganic compounds.

The model for B[a]P distribution in the Ohio River ecosystem proposed by Ryan and Cohen (1986) is a convincing example of the appropriateness of concentrating on the stable, particle-bound portion of the PAH 'spectrum'. This one-dimensional, dynamic, multi-media partitioning model presumes that transport of B[a]P in gaseous or dissolved form is negligible. Its results are in good agreement with observation.

Using actual regional emission and discharge data, Ryan and Cohen's model predicted that by the twelfth year of constant release rates of B[a]P, a "pseudo-steady" state had been reached. More than 99% of the B[a]P mass was predicted to reside in surface soil. Sediment was not a modelled medium, but the Level I fugacity results presented earlier in this section and the Level III calculations presented below suggest that B[a]P would likely partition to both surface soil and sediment.

The excellent agreement between the predictions of the Ryan and Cohen model and reported local measurements of the various media suggests that the long-term partitioning of B[a]P in similar multi-media environments, such as the Great Lakes Basin, would strongly favour soil and sediments. The same fate would be expected for PAH with physical and chemical properties similar to those of B[a]P.

The relatively simple static input-output mass balance model of Strachan and Eisenrich (IJC 1987, 1988) also focusses on B[a]P as representative of PAH and also presumes that vapour-phase B[a]P is not important. Since this model uses observed environmental concentrations as inputs, it cannot be calibrated against these data.

Cupitt (1980) also presumes that only particulate B[a]P (again, representing PAH, or more generally, polycyclic organic matter) is important in determining fate and atmospheric residence time.

Mackay and Paterson (1988) have carried out advanced Level III fugacity modelling for B[a]P in an environment defined by the conditions and dimensions of southern Ontario. This model incorporates detailed advection, degradation and intermedia transfer rates, as well as estimated emission (discharge) rates to air, water and soil. It also predicts that the predominant steady-state partitioning is to soil and sediments. That is, the equilibrium partitioning predicted by the lower-level fugacity models is confirmed by the higher-level models incorporating kinetics.

For example, the Level I and Level III models for B[a]P predict the following distributions (%):

	Air	Water	Soil	Sediment
Level I	0	0.2	52	48
Level III	0.1	5	72	23

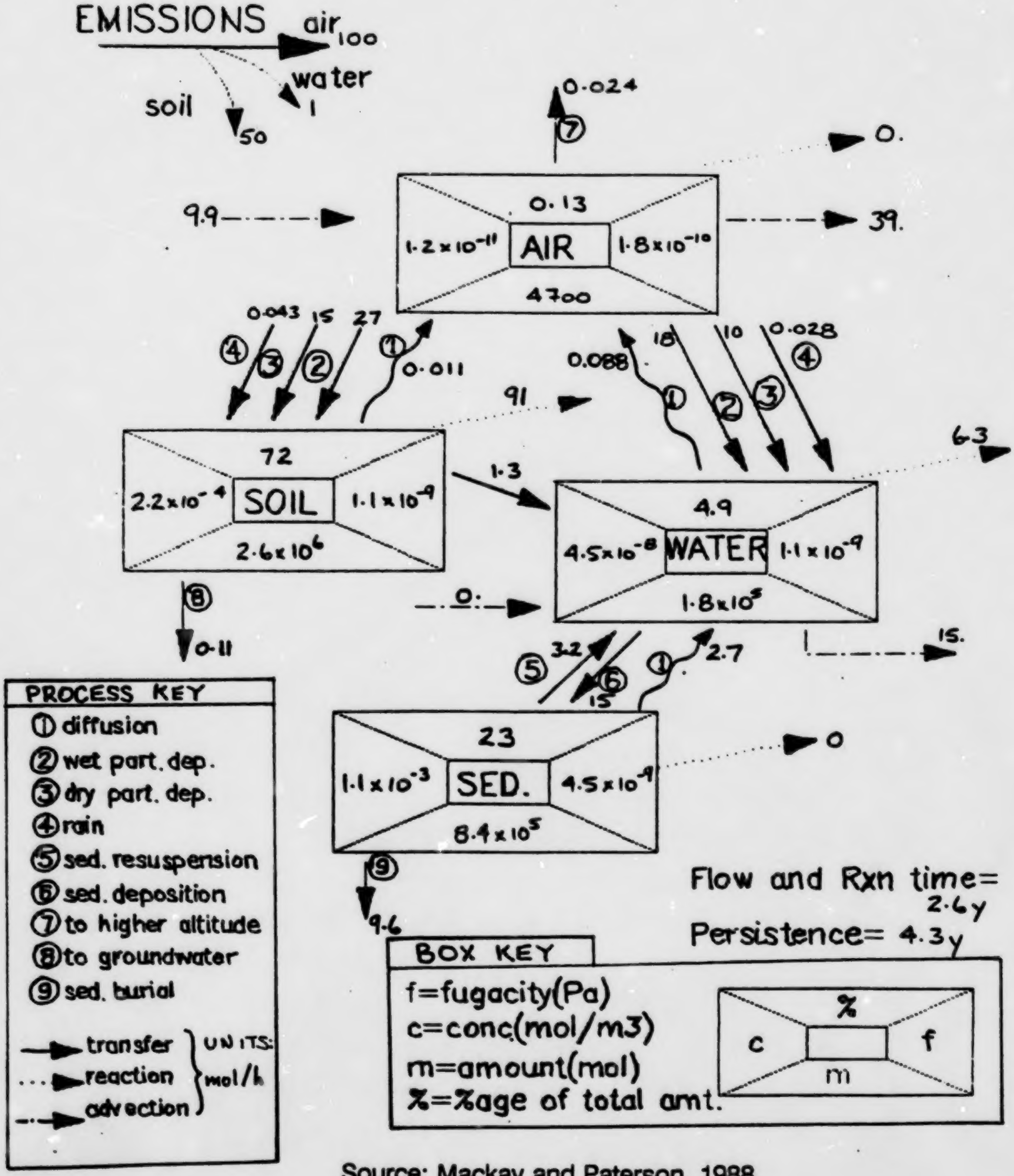
That is, the predictions of the different levels of fugacity modelling are similar. This general agreement lends credibility to the use of the Level I calculations for comparing the environmental behavior of the other PAH. Mackay, Paterson and Schroeder (1986) show how the detailed processes of air-water interchange of contaminants can be incorporated into a fugacity-based model, to account for a physically realistic detailed partitioning to airborne particles and precipitation, for example. Mackay et al. (1986) address substances with properties similar to PAH. Mackay and Paterson (1988) include these detailed processes, as well as intermedia exchanges involving soil and sediment, as shown in Figure 8-1. This figure is explained below.

In summary, equilibrium and dynamic modelling exercises which have been carried out for B[a]P for this study and elsewhere (as described above) consistently predict that this compound resides ultimately in soils and (buried) sediments. B[a]P is intermediate in properties which determine environmental fate in the PAH family, and may, therefore, be considered typical. In the latter medium, this typical PAH, presumably, undergoes mineralization or biotransformation over a very long period of time. The atmosphere and aquatic media, then, serve as vectors for transport of PAH to soils and sediments and do not act as cumulative reservoirs for PAH.

Figure 8-1, which is based on the work by Mackay and Paterson (1988) referred to above, shows a calculated mass balance for B[a]P in the Great Lakes Basin (southern Ontario) from advanced Level III fugacity modelling. The key to the figure indicates the definitions of the processes and quantities for "emissions" (includes discharges to air, water and soil), amounts advected, transferred to various media or ultimate residences (sinks), and amounts degraded by reaction. The report by Mackay and Paterson (1988 and W. Stiver, private communication, 1988) should be consulted for detailed explanation.

FIGURE 8-1

Level III Fugacity Model
Results for B[a]P in Ontario


EMISSIONS
air 100
water 1
soil 50
0.024
⑦
0.
9.9
0.13
AIR
1.2×10⁻¹¹
1.8×10⁻¹⁰
4700
39.
0.043
15
27
④
③
②
①
0.011
0.088
18
10
0.028
91
6.3
72
SOIL
2.2×10⁻⁴
1.1×10⁻⁹
2.6×10⁶
1.3
4.9
WATER
4.5×10⁻⁸
1.1×10⁻⁹
1.8×10⁵
0:
⑧
0.11
3.2
⑤
⑥
15
2.7
15.
23
SED.
1.1×10⁻³
4.5×10⁻⁹
8.4×10⁵
0
⑨
9.6
Flow and Rxn time= 2.6y
Persistence= 4.3y
PROCESS KEY
① diffusion
② wet part. dep.
③ dry part. dep.
④ rain
⑤ sed. resuspension
⑥ sed. deposition
⑦ to higher altitude
⑧ to groundwater
⑨ sed. burial
transfer
reaction
advection
UNITS: mol/h
BOX KEY
f=fugacity(Pa)
c=conc(mol/m3)
m=amount(mol)
%=%age of total amt.
%
c
f
m

Source: Mackay and Paterson, 1988.

The figure is used here to indicate that accounting for all of the major environmental processes produces a picture of B[a]P transformation and fate - ultimate movement toward soil and sediment - that is consistent with other evidence presented.

Some additional explanation may help to clarify the information presented in Figure 8-1. The key to the data boxes (calculated results) for each compartment (air, soil, water and sediment) appears in the lower right hand corner. The key to the process arrows is in the lower left hand corner. The circled numbers written next to each process arrow identify the process (see Key). The other numbers written next to each process arrow are the calculated rates (mol/h) of chemical removal from the compartment by the indicated process.

Note that chemical reaction rates of removal from both air and sediment are taken to be zero in this model. This assumption implies that the rates of other removal processes are much more significant than chemical reaction in these compartments. Based on current knowledge, the assumption seems reasonable. With reference to the atmospheric compartment, zero chemical raction rate means that the PAH emitted in Ontario are normally transported (advected) out of Ontario before significant chemical transformation occurs.

To summarize, Figure 8-1 shows that for the 100 mol/h of B[a]P emitted to the air in Ontario, approximately 70 mol/h (70%) are deposited to water and soil in Ontario and 30 mol/h (30%) remain in the air to be added to the "background" influx of 10 mol/h, producing a net flux out of the Province of about 40 mol/h. The out flux, of course, impinges on downwind areas. The results shown in Figure 8-1 imply that Ontario emissions (which include discharges) produce an approximately fourfold increase in airborne flux of B[a]P (and by extrapolation, of PAH) and an approximately three-fold increase in airborne concentration (1 ng m^{-3} to 3ng m^{-3} for B[a]P). The latter value is high compared with current monitoring data.

The atmosphere, thus, does not appear to be a reservoir for B[a]P, and by analogy, for other PAH with similar physical and chemical properties. The 'emission' quantities used by Mackay and Paterson (1988) are not entirely consistent with quantities estimated in the present work; for example, the air emission corresponds to 200 MT/y B[a]P compared with Concord's estimate of 250 MT/y for total PAH from major sources. These numbers are considered to be comparable, within the current quality of data. The Mackay and Paterson (1988) estimate of 200 MT/y B[a]P emissions to air predict ambient air concentrations which are higher than observed; therefore, a better estimate would probably be a factor of at least three lower. That is, an estimated emission of 50 MT (B[a]P)/y would bring the predictions of the Level III model more in line with observation. Such a number would be more consistent with the estimated total PAH emission for Ontario shown in Table 3-31. The soil emission rate shown in Figure 8-1 is estimated to account for spillage of fuels and lubricants, which contain PAH both as used and as a result of aging processes in use. The supporting data for the Level III calculation are provided in detail in Appendix A.

Thus, the information presented in previous chapters, implies that, within present uncertainties of physical and chemical properties and environmental concentrations, it is wise to focus on PAH which are predominantly associated with airborne particulate matter and soils or sediments for the purposes of evaluating and tracing source impacts. Within that subset of PAH, those with the lowest vapour pressure (highest affinity for airborne particulate matter) and least chemical reactivity are likely to be the most unambiguously traceable in the environment.

Toxicologically, the higher molecular weight PAH predominating in particulate matter include most of the demonstrated or suspect carcinogens (see Table 2-2), and particle-bound PAH will have greater absorptivity in the human respiratory system, the hydrophobic vapour-phase PAH having less affinity for epithelial tissue (and, therefore, less tendency to be available for absorption).

For the above reasons, the estimates of emission rates and atmospheric concentrations which are described in the following sections focussed on particulate emissions and particle-bound PAH.

8.5 Emission Rate Estimates

Province-wide PAH emissions were estimated based on the Ministry of the Environment's current emission inventory (1984, 1985 data) of particulate matter from combustion processes and other PAH sources, by applying best available estimates of PAH emission factors for a number of individual PAH.

Estimates of background and source-influenced ambient PAH concentrations in Ontario will assist in the establishment of regulatory approaches for PAH. In the context of this report, background levels will distinguish between the 'clean air' levels and those attributable to long range mesoscale transport (LRT). Knowledge of the relative magnitudes of the LRT-influenced and the local source-influenced PAH levels will provide guidance for selecting regulatory approaches and, if necessary, control strategies. In order to obtain these estimates, a preliminary emissions inventory for Ontario has been developed, and the contributions of PAH sources to ambient TSP levels in a selected area of Ontario (Hamilton) were estimated. In addition, estimates of the background levels of PAH as a result of long range transport were made. The assessment of these estimates in terms of their reliability, the need for their refinement and their implications for policy regarding PAH in Ontario are discussed.

8.5.1 Estimation of Ambient PAH Concentration for Hamilton

Rough dispersion model estimates of the annual mean ambient PAH concentrations in the Hamilton area were made. The dispersion model also provided estimates of the proportions of the total TSP concentration contributed by coke ovens as well as all steel operations. The model estimates for the contributions of the steel operation sources were compared with similar estimates obtained by dispersion and receptor modelling based on 1979 emissions data (ORF et al., 1982). Estimates of the particulate PAH concentration in Hamilton were derived by assuming PAH emission factors for certain compounds. These data provide the basis for estimating ambient PAH concentrations.

The Industrial Source Complex Long Term (ISCLT) model was used. Model inputs included emissions from point and area sources in the Hamilton area, and meteorological data from Toronto Airport were used as model inputs. The point and area sources used were the same as those in the Hamilton road dust study (ORF et al., 1982). Two sets of emission rates from these sources were considered: 1979 particulate emission rates which are identical to those used in the road dust study, and 1984 particulate emission rates based on the most recent TSP emissions inventory. For the 1984 data, since detailed coke oven particulate data were not available, the following assumptions were made:

- the total emissions from sources in the area modelled were set to 2400 tonnes (in the 1984 EI, the grid total for particulate emissions is 2477 MT);

- since some coke oven and other major point sources in the grid had been reduced between 1974 and 1979, those sources which had not been reduced between 1974 and 1979 were arbitrarily reduced in order to agree with the total emissions as given in the 1984 EI: the latter were 2400 T, with 1000 T from coke ovens and 1400 T from other sources;

- the line sources used in the Hamilton road dust study were replaced with a traffic area source whose strength was based on the 1984 EI data for gasoline and diesel sources in the grid. The emissions in the model domain were prorated by area according to the following relationship: traffic emissions in model domain = grid area traffic source x (model domain area / grid area).

Estimates of the total TSP concentration for all sources, as well as the separate TSP concentration attributable to the coke ovens, traffic and the remaining sources were calculated. The estimates of TSP from the coke oven and automobile sources together with emission factors of PAH compounds from these sources will allow the estimation of ambient PAH concentrations. The source emissions data are presented in Table 8-8.

TABLE 8-8

Point Source Emission Inventory for Hamilton

Source	Description	TSP (MT/yr) 1974	1979	1984
1	Canron Ltd.	119.0	108	50
2	Stelco Steam Plant	92.9	20	6
3	Stelco Blast Furance	637.4	496	150
4	Stelco Coke Quench	145.7	132	70*
5	Stelco Sinter Plant	1372.2	1131	375
6	Stelco Coke Ovens	930.6	803	450*
7	Stelco Coal Handling	445.1	418	92
8	Stelco B.O.F.	450.3	495	109
9	Stelco Open Hearth	803.3	568	150
10	Proctor & Gamble	234.9	351	150
11	Dofasco B.O.F.	1125.8	459	150
12	Dofasco Coke Oven	659.9	557	300*
13	Dofasco Blast Furnace	448.3	368	100
14	Dofasco Coke Oven	560.8	181	180*
15	National Steele Can.	89.6	81	18
16	Interflow Systems	181.4	181	50
Total		8297.2	6369	2400

* Coke total 1000 MT
Grid # 295

Ambient annual TSP concentrations were estimated at four receptor locations (the same as those used in the Hamilton road dust study). The model predictions for the total annual mean TSP and the portion of the annual mean TSP attributed to the coke ovens, traffic and other sources are listed in Table 8-9.

The model predictions of the annual mean TSP concentration may be compared with observation at monitoring sites in Hamilton during similar years. The 1979 annual mean TSP concentrations at the modelled receptor sites were in the range 70 to 93 ug m^{-3}.

The model estimates determined in this study did not include any contribution from background sources. This background level would be equivalent to TSP measurements made at remote Ontario sites.

The Hamilton study included a background site and TSP measurements, and estimates for the background site were of the order of 40 ug/m^3 (ORF et. al. 1982). The 1984 prediction of the annual mean can be compared only with the MOE monitoring data for Barton/Sanford (MOE station 29025) for which the annual mean in 1984 was 81 ug/m^3. The model predictions (42 to 48 ug/m^3) plus an assumed level of 40 ug/m^3 for the background, produce agreement with the observations to within 25%. Such agreement is as good as can be achieved for these types of data and the inherent uncertainties of modelling area sources.

TABLE 8-9

Summary of Modelling Results
ISCLT Model Predictions for 1979 and 1984
For the Hamilton Area

Annual Mean TSP concentrations
(ug/m^3)

Year	Receptor	Coke Ovens	Traffic Diesel	Traffic Gasoline	Other Sources	Total	Observed (2)
1979	E	2.0	0.4	2.6	40	45	65-81
	J	2.1	0.5	3.3	36	42	93
	C	2.7	0.5	3.3	38	44	70-84
	O	3.0	0.4	3.2	41	48	89
1984	E	1.13	0.36	2.59	38	41	
	J	1.19	0.47	3.34	36	38	
	C	1.52	0.46	3.28	33	44	
	O	1.67	0.44	3.16	39	44	

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(2) ORF, 1982. Range of observed values at the different sites are annually adjusted averages.

The percentage contribution of the coke ovens to TSP levels is estimated at between 3 and 4% by mass based on the current model runs (Table 8-10). This percentage may be compared with receptor model and dispersion model predictions for the contributions of the iron and steel sources in Hamilton from ORF et al., 1982. These contributions were estimated at 8 and 6%, respectively, but include all point sources and not just the coke oven sources. The agreement is reasonable given the assumptions made.

8.6 Estimate of the LRT contribution to PAH levels in Ontario

The dispersion modelling or receptor modelling estimates provide preliminary estimates of the ambient levels of PAH due to local sources. Previous receptor model estimates of the background TSP levels are reasonable, and may be taken as an upper limit for the contribution from distant, i.e., LRT sources.

In order to estimate the PAH concentration contributed by LRT sources, the constancy of the PAH/TSP ratio for each source will be assumed to apply to the background measurements. However, it must be noted that chemical transformation of PAH may render the use of the same PAH/TSP ratio in sources as in ambient measurements to be strictly inappropriate. For example, the B[a]P/TSP ratios near PAH industrial and urban sources were between 5 and 66 ug/g, while at remote sites, the ratio was 0.3 to 0.6 ug/g (Gibson, 1986). Analogous ratios for 1-nitropyrene were lower at urban/industrial sites (0.2 to 0.6 ug/g) than at the remote sites (0.5) (Gibson, 1986).

TABLE 8-10

Percentage Contribution to TSP from Coke Ovens, Traffic and Other Sources in Hamilton

Year	Receptor	Coke Ovens	Traffic Diesel	Traffic Gasoline	Other Sources
1979	E	4.3	0.8	5.8	89.1
	J	4.9	1.1	8.0	86.0
	C	6.0	1.0	7.4	85.6
	O	6.2	0.9	6.6	86.2
1984	E	2.8	0.9	6.3	92.7
	J	3.1	1.2	8.7	94.1
	C	3.4	1.0	7.4	74.5
	O	3.8	1.0	7.2	88.6

If it is assumed that the PAH/TSP ratio, in particular, the B[a]P/TSP and the total PAH/TSP ratios for Ontario emissions of 2 x 10^{-5} and 0.015 respectively, are similar to the ratios in LRT sources, then the B[a]P and total PAH concentrations in background TSP would be of the order of 0.8 and 600 ng/m^{3}, respectively, assuming a background TSP level of 40 ug/m^{3}. The B[a]P estimates do not take into account the degradation of B[a]P during transport. The B[a]P/TSP ratio can be up to 240 times greater at near-source sites than at remote sites (Gibson 1986). A more appropriate background B[a]P level applicable to remote Ontario locations would therefore be about 4 pg m^{-3} assuming a factor of 200 for the B[a]P/TSP ratio near sources relative to remote sites.

Background measurements of PAH in Ontario are not available since most PAH sampling has been done in urban locations. The most representative urban sites at which ambient PAH data are available are for Sudbury and Niagara-on-the-lake where B[a]P levels were 0.1 to 0.4 ng m^{-3} (Katz et al., 1978) and 0.4 ng m^{-3} (Hoff and Chan, 1987), respectively. Measurements made at a remote site in Bermuda (Gibson, 1986; Gibson and Wolff, 1985) may be used to provide some indication of the impact of LRT from U.S. sources on Ontario. The distance between U.S. emission sources and Ontario is similar to the distance between the east coast of the U.S. and Bermuda, but the absence of additional sources in the ocean trajectory undoubtedly alters the chemistry and concentrations relative to the two receptor areas (i.e., Bermuda and Ontario). The nitro-PAH levels in Bermuda were in fact higher than B[a]P when there was LRT from U.S. sources. This reflects the atmospheric transformation of B[a]P, the formation of nitroPAH during transport and possibly the stability of the nitroPAH, although they are somewhat reactive photochemically. B[a]P and 1-nitropyrene concentrations at the remote Bermuda site were, respectively, about 5 and 10 pg/m^3 with TSP levels of about 20 ug/m^3 (Gibson, 1986). The B[a]P measurements are similar to those estimated above. If similar levels apply to air masses entering Ontario, then more emphasis must be placed on establishing the concentrations of the stable PAH, e.g., B[e]P, as well as the secondary PAH compounds, namely nitro- and oxy- PAH formed during transport.

Air masses entering Ontario may be considered as either "background" or "polluted". The former would include air masses such as those crossing the western border with Manitoba and those segments of the southern border with the U.S. that include Lakes Superior, Huron, and Erie. For purposes of estimating the flux into Ontario, it is convenient to consider a straight line strictly from Buffalo to Thunder Bay across which air masses move. That segment of the line from Buffalo to the shore of Lake Huron (300 km) may be considered to bear higher B[a]P levels (approximately 0.8 ng/m^3) in air masses which would enter southern Ontario. The remaining segment from the shore of Lake Huron to Thunder Bay (approximately 850 km) would bear background B[a]P levels (4 pg/m^3). The fluxes crossing these segments are calculated from the following equation (see Galloway and Whelpdale, 1980):

$$F = c\,u\,H\,L\,f$$

where c is the mean PAH concentration, u the mean annual wind speed (7 ms^{-1}), H is the mean annual mixing height (900 m) and L is the length of the boundary bearing the flux and f is the fraction of the time winds blown across the boundary (assumed to be 1.0). The annual amount of B[a]P entering southern Ontario is estimated at 1.5 g/s or 47.7 tonne/y. Estimates for the remainder of the boundary are 0.68 tonnes/year.

The estimated B[a]P flux entering southern Ontario is significant, corresponding to approximately 50% of the total Ontario B[a]P emissions. A more realistic estimate of this flux will consider the frequency with which winds blow across the 300 km segment. Including this frequency (approximately 60% of the time) will reduce the B[a]P entering Ontario to approximately 29 tonnes/year - an amount which is still significant, relative to the total B[a]P emissions in Ontario. That is, for southern Ontario, imported PAH appear to dominate emissions within the Povince; whereas, for northern Ontario, the opposite obtains.

Amount entering southern Ontario:

$$\frac{0.8 \times 7.0 \times 900 \times 300 \times 10^3}{10^9 \times 10^3 \times 10^3}$$

$\times (60 \times 60 \times 24 \times 365) = 47.7$ tonnes

Amount entering the remainder of Ontario.

$0.004 \times 7 \times 850 \times 10^3 \times 900 \times 60 \times 60 \times 24 \times 365$

$10^9 \times 10^6 = 0.67$ tonnes

8.7 Regional Estimates for PAH Emissions in Ontario

A regional PAH emissions inventory was developed for Ontario by using the total suspended particulate (TSP) emissions inventory developed by the MOE which includes the six major types of PAH sources in Ontario. These include the following point sources:

- forest fires;
- gasoline fuelled vehicles;
- diesel fuelled vehicles;
- residential wood fireplaces and stoves;
- coke ovens; and
- coal fired thermal generating stations.

The PAH composition for each of the source types includes 22 of the 47 PAH compounds that were considered in this report. Selection was contingent on a reported PAH emission factor for at least 3 of the 6 sources. A collective estimate was used for each group of isomers and were identified under generic names. For example, under the generic name of benzofluoranthenes would be included the benzo[b] and benzo[k]fluoranthene isomers. Emission factors, F_{np}, for the 22 compounds are presented in Table 8-14. The total PAH emission in each grid was taken as the sum of the emissions of the twenty-two compounds for all six sources (equation 8.2).

$$E_g = \sum_{n=1,\, p=1}^{n=6,\, p=22} E_{npg} \qquad 8.2$$

Also included in the emission inventory are the estimated contributions for sources discharging to water and to soil in southwestern Ontario. These data are provided as Maps labelled B1-1 to B1-4 in Appendix B of this report.

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APPENDIX A

Level 3 Fugacity Model Data

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date: 03-22-1988          time: 09:02:22

                          LEVEL 3 FUGACITY MODEL  - B[a]P

Predicted fate of Benzo(a)pyrene in Southern Ontario

compound properties

molecular weight                     252.30  g/mol
aqueous solubility                     3.8000E-03  g/m3  or    1.5061E-05  mol/m3
vapour pressure                        7.3000E-07  pa    or    7.2045E-12  atm  or   5.4755E-09   mm Hg
henry's constant                       4.8468E-02 pa m3/mol
octanol-water part coeff (log)          5.98
temperature                           25.0  deg C  or    298.2  K

bulk compartment              volume       height/        area           Z          density
                                m3         depth (m)       m2        mol/m3.Pa       kg/m3

 1  bulk air                4.000E+14     2.000E+03    2.000E+11     6.672E-02         1.19
 2  bulk water              4.000E+12     5.000E+01    8.000E+10     4.101E+01      1000.01
 3  bulk soil               1.200E+10     1.000E-01    1.200E+11     1.944E+05      1500.24
 4  bulk sediment           8.000E+08     1.000E-02    8.000E+10     2.332E+05      1420.00

total area (m2)   2.000E+11

subcompartment                volume         Z          density    mass fraction      volume
                                m3       mol/m3.Pa      kg/m3    organic content    fraction

1, 1   air                  4.000E+14    4.034E-04       1.19                      1.00E+00
1, 3   air particles        8.000E+03    3.316E+09    2400.00                      2.00E-11

2, 2   water                4.000E+12    2.063E+01    1000.00                      1.00E+00
2, 3   water particles      2.000E+07    3.887E+06    2400.00         0.20         5.00E-06
2, 4   biota                4.000E+06    9.458E+05    1000.00                      1.00E-06

3, 1   soil air             2.400E+09    4.034E-04       1.19                      2.00E-01
3, 2   soil water           3.600E+09    2.063E+01    1000.00                      3.00E-01
3, 3   soil solids          6.000E+09    3.887E+05    2400.00         0.02         5.00E-01

4, 2   pore water           5.600E+08    2.063E+01    1000.00                      7.00E-01
4, 3   sed. solids          2.400E+08    7.774E+05    2400.00         0.04         3.00E-01
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Reaction Parameters

 bulk compartments               rate constant  half-life      D value
                                     h-1            h          mol/pa.h

 1  bulk air                     0.0000E+00     0.0000E+00     0.0000E+00
 2  bulk water                   3.5000E-05     1.9800E+04     5.7419E+09
 3  bulk soil                    3.5000E-05     1.9800E+04     8.1632E+10
 4  bulk sediment                0.0000E+00     0.0000E+00     0.0000E+00

 Subcompartments

1, 1   air                       0.0000E+00     0.0000E+00     0.0000E+00
1, 3   air particles             0.0000E+00     0.0000E+00     0.0000E+00

2, 2   water                     0.0000E+00     0.0000E+00     0.0000E+00
2, 3   water particles           0.0000E+00     0.0000E+00     0.0000E+00
2, 4   biota                     0.0000E+00     0.0000E+00     0.0000E+00

3, 1   soil air                  0.0000E+00     0.0000E+00     0.0000E+00
3, 2   soil water                0.0000E+00     0.0000E+00     0.0000E+00
3, 3   soil solids               0.0000E+00     0.0000E+00     0.0000E+00

4, 2   pore water                0.0000E+00     0.0000E+00     0.0000E+00
4, 3   sed. solids               0.0000E+00     0.0000E+00     0.0000E+00

Advective Parameters

compartment                 flow        inflow concn   rate constant    D value      residence time
                            m3/h          mol/m3           h-1          mol/pa.h           h

 1  bulk air              3.30E+12      3.00E-12        8.25E-03        2.20E+11       1.21E+02
 2  bulk water            3.30E+08      0.00E+00        8.25E-05        1.35E+10       1.21E+04
 3  bulk soil             0.00E+00      0.00E+00        0.00E+00        0.00E+00      infinity
 4  bulk sediment         0.00E+00      0.00E+00        0.00E+00        0.00E+00      infinity

Transfer to higher altitude,sediment burial and leaching from soil to groundwater

process                 velocity        velocity      flow        rate constant    D value              residence times
                         m/y            m/h           m3/h           h-1           mol/pa.h           h                y

transfer to higher alt  9.00E+01        1.03E-02      2.05E+09      5.14E-06       1.37E+08       1.95E+05         2.22E+01
leaching from soil      3.40E-01        3.88E-05      4.66E+06                     9.61E+07
sediment burial         3.00E-04        3.42E-08      2.74E+03      1.14E-05       2.13E+09       8.76E+04         1.00E+01
```

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Transfer parameters between compartments

     Total D Values and Fluxes

     compartment          D            flux        tau(i,j)
                      (mol/h*pa)     mol/h)          h

from   1  to   2     1.605E+11    2.831E+01    1.152E+02
from   2  to   1     9.663E+07   -2.831E+01    1.152E+02


from   1  to   3     2.406E+11    4.259E+01    7.686E+01
from   3  to   1     1.151E+07   -4.259E+01    7.686E+01

from   2  to   4     1.498E+10    9.600E+00    7.588E+03
from   4  to   2     1.493E+09   -9.600E+00    6.977E+03

from   3  to   2    1.161E+09    1.297E+00    1.392E+06

     Individual D Values, Flows and Velocities

     compartments     by                D            flow         flow        velocity      velocity
                                    (mol/h*pa)      (m3/h)       (m3/y)       (m/h)         (m/y)

from   1  to   2     diffusion        9.663E+07
                     rain             1.602E+08    7.763E+06    6.800E+10    9.703E-05    8.500E-01
                     wet deposition   1.030E+11    3.105E+01    2.720E+05    3.881E-10    3.400E-06
                     dry deposition   5.730E+10    1.728E+01    1.514E+05    1.080E+01    3.000E-03 (m/s)

from   2  to   1     diffusion        9.663E+07

from   1  to   3     diffusion        1.151E+07
                     rain             2.402E+08    1.164E+07    1.020E+11    9.703E-05    8.500E-01
                     wet deposition   1.544E+11    4.658E+01    4.080E+05    3.881E-10    3.400E-06
                     dry deposition   8.594E+10    2.592E+01    2.271E+05    1.080E+01    3.000E-03 (m/s)

from   3  to   1     diffusion        1.151E+07

from   2  to   4     diffusion        7.827E+08
                     deposition       1.420E+10    3.653E+03    3.200E+07    4.566E-08    4.000E-04

from   4  to   2     diffusion        7.827E+08
                     resuspension     7.100E+08    9.132E+02    8.000E+06    1.142E-08    1.000E-04

from   3  to   2     water flow       9.609E+07    4.658E+06    4.080E+10    3.881E-05    3.400E-01
                     soil flow        1.065E+09    2.740E+03    2.400E+07    2.283E-08    2.000E-04
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Input Transport Parameters

  Mass Transfer Coefficients (MTC) (m/h)

        Air-Water   air-side MTC               3.00E+00
                    water-side MTC             3.00E-02
                    overall water-side MTC     5.85E-05

        Air-Soil
                    air-side MTC               1.000E+00

        Water-Sediment
                    water-side MTC             1.000E-02

  Diffusivities

air molecular diffusivity   0.40E-01  m2/h     air effective diffusivity 0.75E-03  m2/h   mean path length  0.0500  m
water molecular diffusivity 0.40E-05  m2/h
                    soil                     water effective diffusivity 0.29E-06  m2/h   mean path length  0.0500  m
                    sediment                 water effective diffusivity 0.25E-05  m2/h   mean path length  0.0050  m

  D Values for Diffusive Flow in Soil Air and Water

        Soil   air diffusion               7.286E+05
               water diffusion             1.438E+07

  D Value for Diffusive Flow in Sediment Pore Water

        Sediment   water diffusion         8.217E+08
```

```
Bulk Compartments

compartment                amount      percent                    concentrations                       fugacity
                            mol                    mol/m3          microg/g        microg/m3             Pa

 1  bulk air              4.725E+03      0.130    1.181E-11       2.514E-06       2.980E-03          1.770E-10
 2  bulk water            1.788E+05      4.926    4.470E-08       1.128E-05       1.128E+01          1.090E-09
 3  bulk soil             2.605E+06     71.774    2.171E-04       3.651E-02       5.477E+04          1.117E-09
 4  bulk sediment         8.410E+05     23.170    1.051E-03       1.368E-01       2.652E+05          4.507E-09

    Total                 3.630E+06    100.000

Subcompartments

compartment                amount      percent                    concentrations                       fugacity
                            mol                    mol/a3          microg/g        microg/m3             Pa

1, 1   air                2.857E+01      0.001    7.142E-14       1.520E-08       1.802E-05          1.770E-10
1, 3   air particles      4.696E+03      0.129    5.870E-01       6.171E+01       1.481E+08          1.770E-10

2, 2   water              8.994E+04      2.478    2.248E-08       5.673E-06       5.673E+00          1.090E-09
2, 3   water particles    8.472E+04      2.334    4.236E-03       4.453E-01       1.069E+06          1.090E-09
2, 4   biota              4.123E+03      0.114    1.031E-03       2.600E-01       2.600E+05          1.090E-09

3, 1   soil air           1.081E-03      0.000    4.506E-13       9.591E-08       1.137E-04          1.117E-09
3, 2   soil water         8.297E+01      0.002    2.305E-08       5.815E-06       5.815E+00          1.117E-09
3, 3   soil solids        2.605E+06     71.772    4.342E-04       4.564E-02       1.095E+05          1.117E-09

4, 2   pore water         5.208E+01      0.001    9.299E-08       2.346E-05       2.346E+01          4.507E-09
4, 3   sed. solids        8.410E+05     23.168    3.504E-03       3.684E-01       8.840E+05          4.507E-09




summary of 4 bulk compartment mass balances (mol/h)

                       emissions      inflow          reaction        outflow          net flux out
                                                                                     to other compts

bulk air               1.000E+02     9.900E+00       0.000E+00       3.898E+01         7.090E+01
bulk water             1.000E+00     0.000E+00       6.258E+00       1.475E+01        -2.001E+01
bulk soil              5.000E+01     0.000E+00       9.118E+01       0.000E+00        -4.129E+01
bulk sediment          0.000E+00     0.000E+00       0.000E+00       0.000E+00        -9.600E+00

Total                  1.510E+02     9.900E+00       9.744E+01       5.373E+01


total input (emissions and inflow)       1.609E+02 mol/h
total output (reactions and outflow)     1.609E+02 mol/h

residence time (hours) 22558.97          persistence 37250.86
                (days) 939.9571          persistence 1552.119
```

```
                                        Transfer and Transformation rates (mol/h)

                                   Bulk air          Bulk water        Soil              Sediment          Total

emissions                          1.000E+02         1.000E+00         5.000E+01         0.000E+00         1.510E+02

advective inflow                   9.900E+00         0.000E+00         0.000E+00         0.000E+00         9.900E+00

advective outflow                  3.898E+01         1.475E+01         0.000E+00         0.000E+00         5.373E+01

reaction                           0.000E+00         6.258E+00         9.118E+01         0.000E+00         9.744E+01

transfer to higher altitude        2.427E-02                                                               2.427E-02

leaching from soil                                                     1.073E-01                           1.073E-01

sediment burial                                                                          9.600E+00         9.600E+00

transfer to air from               0.000E+00        -2.831E+01        -4.259E+01         0.000E+00        -7.090E+01

transfer to water from             2.831E+01         0.000E+00         1.297E+00        -9.600E+00         2.001E+01
        by diffusion air-water     1.711E-02
        by diffusion water-air    -1.053E-01
        net diffusion             -8.820E-02
        by rain                    2.835E-02
        by wet deposition          1.823E+01
        by dry deposition          1.014E+01
        by water runoff                                                1.073E-01
        by soil runoff                                                 1.190E+00

transfer to soil from              4.259E+01        -1.297E+00         0.000E+00         0.000E+00         4.129E+01
        by diffusion air-soil      2.038E-03
        by diffusion soil-air     -1.286E-02
        net diffusion             -1.082E-02
        by rain                    4.253E-02
        by wet deposition          2.734E+01
        by dry deposition          1.522E+01

transfer to sediment from          0.000E+00         9.600E+00         0.000E+00         0.000E+00         9.600E+00
        by diffusion water-sediment                  8.530E-01
        by diffusion sediment-water                 -3.528E+00
        net diffusion                               -2.675E+00
        by sediment deposition                       1.547E+01
        by sediment resuspension                    -3.200E+00
```

APPENDIX B

Maps Illustrating PAH Regional Estimates

1.0 PROCEDURE FOR ESTIMATING REGIONAL PAH EMISSIONS

PAH emissions were estimated as follows:

a) Only air emissions were considered from the following sources:
   - o gasoline and diesel-powered mobile sources;
   - o residential wood burning stoves and fireplaces; and
   - o forest fires.

b) The Air Resources Branch (MOE) total suspended particulate (TSP) emissions inventory for each of the 3 sources was used to provide a reference database (MOE Emissions Inventory, 1985).

c) The TSP/PAH ratio was assumed to be approximately constant for each of the three sources.

A summary of the TSP/PAH ratios used for these estimates is presented in Table B1-1. The data correspond to values in Tables 3-23, 3-26 and 3-30.

1.1 Rationale for Source Selection

The three sources used in this analysis contribute approximately 97% of the total annual PAH emissions in Ontario. Thus, although coke oven and coal fired power generating station emissions, for example, will add to certain localized areas, particularly in southwestern Ontario, these latter sources are excluded from the analysis. In support of this approach is the fact that sources discharging to water and soil will also contribute to localized areas in a similar manner. Therefore, as a preliminary analysis,

TABLE B1-1

PAH, TSP Emissions and PAH/TSP Ratios for Forest Fires, Mobile and Residential Wood Heating Sources

	Unleaded Gasoline 3 way & oxid. cat.* (mg/kL)	Diesel Light & Heavy Duty** (mg/kL)	Wood Burning Stoves*** (mg/GJ)	Forest Fires**** (mg/mT)
PAH			3,113	20,900
TSP			823,529	50,525,000
PAH/TSP	0.0023	0.0069	0.0038	0.0004

* From Table 3-23. (Assume ratio for 3 way catalyst is also applicable for oxidation catalyst.)

** From Table 3-23. (Assume ratio for light duty is the same as heavy duty diesel.)

*** From Table 3-26. Total PAH taken as the sum of entries for emissions factors for wood in the Table. TSP data from U.S. EPA PB83-250720, pp. 1.9-3 to 1.10-5.

**** From Table 3-30. Average values quoted.

we have assumed that an assessment of the regional concentrations to the total PAH inventory from forest fires, mobile and residential woodburning stoves and fireplaces will provide an acceptable database: the alternative would be a detailed evaluation for all major sources, which could not be undertaken at this time.

1.2 Illustrative Regional Maps of PAH Emissions

The estimated PAH emissions and densities are presented in Table B1-2 and illustrated in Figures B1-1 to B1-4. The code used for identification of levels is presented in Table B1-3.

TABLE B1-2

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	1	0.0012	0.0060	0.0000	0.01	0.72
10000	2	0.0424	0.0242	0.0000	0.07	6.66
10000	3	0.0168	0.0249	0.0000	0.04	4.18
10000	4	0.0495	0.0412	0.0000	0.09	9.07
10000	5	0.0461	0.0506	0.0000	0.10	9.67
10000	6	0.0012	0.0034	0.0000	0.00	0.46
10000	7	0.1396	0.1534	0.0000	0.29	29.30
10000	8	0.1318	0.0835	0.0000	0.22	21.53
10000	9	0.0297	0.0548	0.0000	0.08	8.45
10000	10	0.0649	0.1032	0.0000	0.17	16.81
10000	11	0.1806	0.1931	0.0000	0.37	37.37
10000	12	0.0502	0.0442	0.0000	0.09	9.44
10000	13	0.0223	0.0775	0.0000	0.10	9.98
10000	14	0.0104	0.0370	0.0000	0.05	4.74
10000	15	0.1175	0.1327	0.0000	0.25	25.01
10000	16	0.0111	0.0427	0.0000	0.05	5.38
10000	17	0.0104	0.0389	0.0000	0.05	4.93
10000	18	0.0099	0.0317	0.0000	0.04	4.17
10000	19	0.0060	0.0147	0.0000	0.02	2.07
10000	20	0.0041	0.0094	0.0000	0.01	1.36

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
2500	21	0.0074	0.0249	0.0000	0.03	12.93
2500	22	0.0889	0.1342	0.0000	0.22	89.21
2500	23	0.0453	0.0491	0.0000	0.09	37.79
2500	24	0.0366	0.0087	0.0000	0.05	18.11
2500	25	0.0276	0.0144	0.0000	0.04	16.79
2500	26	0.0283	0.0155	0.0000	0.04	17.52
2500	27	0.0272	0.0110	0.0000	0.04	15.25
2500	28	0.0272	0.0106	0.0000	0.04	15.10
2500	29	0.0361	0.0076	0.0000	0.04	17.48
2500	30	0.0463	0.0057	0.0000	0.05	20.77
2500	31	0.0124	0.0079	0.0000	0.02	8.15
2500	32	0.0790	0.0654	0.0000	0.14	57.76
2500	33	0.0014	0.0030	0.0000	0.00	1.76
2500	34	0.0840	0.1175	0.0000	0.20	80.63
2500	35	0.4068	0.5371	0.0000	0.94	377.54
2500	36	0.2385	0.2906	0.0000	0.53	211.65
2500	37	0.0140	0.0215	0.0000	0.04	14.23
2500	38	0.0046	0.0140	0.0000	0.02	7.44
2500	39	0.0053	0.0144	0.0000	0.02	7.86
2500	40	0.0847	0.0582	0.0000	0.14	57.17

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
2500	41	0.0094	0.0091	0.0000	0.02	7.40
2500	42	0.0094	0.0091	0.0000	0.02	7.40
2500	43	0.0035	0.0087	0.0000	0.01	4.86
2500	44	0.0018	0.0087	0.0000	0.01	4.21
2500	45	0.0127	0.0064	0.0000	0.02	7.63
2500	46	0.0186	0.0030	0.0000	0.02	8.67
2500	47	0.0325	0.0420	0.0000	0.07	29.76
2500	48	0.2431	0.3190	0.0000	0.56	224.84
2500	49	0.4784	0.6096	0.0000	1.09	435.20
2500	50	0.1197	0.1187	0.0000	0.24	95.35
2500	51	0.0253	0.0382	0.0000	0.06	25.40
2500	52	0.0016	0.0042	0.0000	0.01	2.31
2500	53	0.0028	0.0060	0.0000	0.01	3.52
10000	54	0.0601	0.0197	0.0000	0.08	7.97
10000	55	0.0088	0.0212	0.0000	0.03	2.99
10000	56	0.0069	0.0174	0.0000	0.02	2.43
10000	57	0.0923	0.0310	0.0000	0.12	12.33
10000	58	0.2711	0.2400	0.0000	0.51	51.10
10000	59	0.1319	0.0877	0.0000	0.22	21.96
10000	60	0.0083	0.0231	0.0000	0.03	3.13

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
2500	61	0.0012	0.0023	0.0000	0.00	1.37
2500	62	0.0016	0.0045	0.0000	0.01	2.46
2500	63	0.0005	0.0015	0.0000	0.00	0.79
2500	64	0.0016	0.0045	0.0000	0.01	2.46
10000	65	0.0088	0.0223	0.0000	0.03	3.11
10000	66	0.2368	0.2328	0.0000	0.47	46.96
10000	67	0.0219	0.0223	0.0000	0.04	4.42
10000	68	0.0576	0.0673	0.0000	0.12	12.48
10000	69	0.0028	0.0068	0.0000	0.01	0.96
2500	70	0.0005	0.0015	0.0000	0.00	0.79
2500	71	0.0016	0.0045	0.0000	0.01	2.46
2500	72	0.0014	0.0026	0.0000	0.00	1.61
2500	73	0.0016	0.0045	0.0000	0.01	2.46
10000	74	0.0083	0.0204	0.0000	0.03	2.87
10000	75	0.0088	0.0231	0.0000	0.03	3.18
10000	76	0.0417	0.0370	0.0000	0.08	7.87
10000	77	0.0428	0.0106	0.0000	0.05	5.34
10000	78	0.0371	0.0163	0.0000	0.05	5.33
10000	79	0.0041	0.0076	0.0000	0.01	1.17
2500	80	0.0083	0.0147	0.0000	0.02	9.21

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
2500	81	0.0005	0.0015	0.0000	0.00	0.79
2500	82	0.0025	0.0053	0.0000	0.01	3.13
10000	83	0.0147	0.0155	0.0000	0.03	3.02
10000	84	0.0382	0.0106	0.0000	0.05	4.88
10000	85	0.0693	0.0272	0.0000	0.10	9.65
10000	86	0.0417	0.0299	0.0000	0.07	7.15
10000	87	0.0018	0.0034	0.0000	0.01	0.52
10000	88	0.0060	0.0079	0.0000	0.01	1.39
10000	89	0.0060	0.0076	0.0000	0.01	1.35
10000	90	0.0060	0.0076	0.0000	0.01	1.35
2500	91	0.0012	0.0019	0.0000	0.00	1.22
2500	92	0.0272	0.0397	0.0000	0.07	26.74
2500	93	0.1020	0.1417	0.0000	0.24	97.49
10000	94	0.0083	0.0204	0.0000	0.03	2.87
10000	95	0.0687	0.0525	0.0000	0.12	12.12
10000	96	0.0055	0.0129	0.0000	0.02	1.84
2500	97	0.0014	0.0030	0.0000	0.00	1.76
2500	98	0.0016	0.0042	0.0000	0.01	2.31
2500	99	0.0016	0.0042	0.0000	0.01	2.31
10000	100	0.1145	0.0257	0.0000	0.14	14.02

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	101	0.0147	0.0212	0.0000	0.04	3.59
10000	102	0.0182	0.0121	0.0000	0.03	3.03
10000	103	0.0573	0.0265	0.0000	0.08	8.38
10000	104	0.0534	0.0110	0.0000	0.06	6.44
10000	105	0.0085	0.0136	0.0000	0.02	2.21
10000	106	0.0286	0.0518	0.0000	0.08	8.03
10000	107	0.0143	0.0231	0.0000	0.04	3.73
10000	108	0.0106	0.0166	0.0000	0.03	2.72
10000	109	0.0180	0.0333	0.0000	0.05	5.12
10000	110	0.0159	0.0215	0.0000	0.04	3.74
10000	111	0.0177	0.0227	0.0000	0.04	4.04
10000	112	0.0117	0.0151	0.0000	0.03	2.69
10000	113	0.0000	0.0000	0.0000	0.00	0.00
2500	114	0.0012	0.0019	0.0000	0.00	1.22
2500	115	0.0016	0.0049	0.0000	0.01	2.61
2500	116	0.0016	0.0049	0.0000	0.01	2.61
10000	117	0.0083	0.0204	0.0000	0.03	2.87
10000	118	0.0030	0.0076	0.0000	0.01	1.06
10000	119	0.0039	0.0083	0.0000	0.01	1.22
2500	120	0.0025	0.0057	0.0000	0.01	3.28

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
2500	121	0.0025	0.0057	0.0000	0.01	3.28
10000	122	0.0044	0.0091	0.0000	0.01	1.34
10000	123	0.0044	0.0076	0.0000	0.01	1.19
10000	124	0.0322	0.0393	0.0000	0.07	7.15
10000	125	0.0090	0.0147	0.0000	0.02	2.37
10000	126	0.0732	0.0257	0.0000	0.10	9.89
10000	127	0.0253	0.0159	0.0000	0.04	4.12
10000	128	0.3567	0.3738	0.0000	0.73	73.05
10000	129	0.0161	0.0268	0.0000	0.04	4.30
10000	130	0.1691	0.1005	0.0000	0.27	26.97
10000	131	0.0117	0.0200	0.0000	0.03	3.18
10000	132	0.0159	0.0215	0.0000	0.04	3.74
10000	133	0.0177	0.0227	0.0000	0.04	4.04
10000	135	0.0000	0.0000	0.0000	0.00	0.00
10000	136	0.0071	0.0000	0.0000	0.01	0.71
10000	137	0.2064	0.2532	0.0000	0.46	45.96
2500	138	0.0041	0.0094	0.0000	0.01	5.44
2500	139	0.0041	0.0094	0.0000	0.01	5.44
10000	140	0.0173	0.0412	0.0000	0.06	5.85
10000	141	0.0092	0.0200	0.0000	0.03	2.92

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	142	0.0046	0.0102	0.0000	0.01	1.48
2500	143	0.0044	0.0106	0.0000	0.01	5.98
2500	144	0.0044	0.0106	0.0000	0.01	5.98
10000	145	0.0081	0.0193	0.0000	0.03	2.73
10000	146	0.0044	0.0072	0.0000	0.01	1.16
10000	147	0.0074	0.0121	0.0000	0.02	1.95
10000	148	0.0308	0.0223	0.0000	0.05	5.31
10000	149	0.0189	0.0287	0.0000	0.05	4.76
10000	150	0.0948	0.0231	0.0000	0.12	11.79
10000	151	0.0180	0.0302	0.0000	0.05	4.82
10000	152	0.0226	0.0393	0.0000	0.06	6.19
10000	153	0.0147	0.0246	0.0000	0.04	3.93
10000	154	0.0046	0.0079	0.0000	0.01	1.25
10000	155	0.1808	0.1999	0.0000	0.38	38.07
10000	156	0.0263	0.0378	0.0000	0.06	6.41
10000	157	0.1071	0.1988	0.0000	0.31	30.59
10000	158	0.2853	0.2169	0.0000	0.50	50.23
10000	160	0.0094	0.0000	0.0000	0.01	0.94
10000	161	0.0030	0.0083	0.0000	0.01	1.13
10000	162	0.0035	0.0102	0.0000	0.01	1.37

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
2500	163	0.0041	0.0094	0.0000	0.01	5.44
2500	164	0.0044	0.0106	0.0000	0.01	5.98
10000	165	0.0237	0.0809	0.0000	0.10	10.46
10000	166	0.0735	0.0752	0.0000	0.15	14.87
10000	167	0.0058	0.0129	0.0000	0.02	1.86
2500	168	0.0129	0.0537	0.0000	0.07	26.63
2500	169	0.0088	0.0329	0.0000	0.04	16.65
10000	170	0.0405	0.0299	0.0000	0.07	7.04
10000	171	0.0359	0.0094	0.0000	0.05	4.54
10000	172	0.1921	0.1262	0.0000	0.32	31.84
10000	173	0.0633	0.0344	0.0000	0.10	9.77
10000	174	0.0401	0.0276	0.0000	0.07	6.76
10000	175	0.7822	0.7185	0.0000	1.50	150.06
10000	176	1.2158	1.0730	0.0000	2.29	228.88
10000	177	0.1008	0.0359	0.0000	0.14	13.67
10000	178	0.1206	0.0283	0.0000	0.15	14.89
10000	180	0.0194	0.0329	0.0000	0.05	5.22
10000	181	0.0191	0.0325	0.0000	0.05	5.16
10000	182	0.0000	0.0000	0.0000	0.00	0.00
10000	183	0.0000	0.0000	0.0000	0.00	0.00

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	184	0.0000	0.0000	0.0000	0.00	0.00
10000	185	0.0369	0.0011	0.0000	0.04	3.80
10000	186	0.0094	0.0268	0.0000	0.04	3.63
10000	187	0.0094	0.0268	0.0000	0.04	3.63
10000	188	0.0064	0.0185	0.0000	0.02	2.50
10000	189	0.1269	0.1618	0.0000	0.29	28.87
10000	190	0.0000	0.0000	0.0000	0.00	0.00
10000	191	0.0000	0.0000	0.0000	0.00	0.00
10000	192	0.1271	0.1183	0.0000	0.25	24.54
10000	193	0.0000	0.0000	0.0000	0.00	0.00
10000	194	0.2966	0.2649	0.0000	0.56	56.15
10000	195	0.0000	0.0000	0.0000	0.00	0.00
10000	196	0.1716	0.2729	0.0000	0.44	44.44
2500	197	0.0120	0.0624	0.0000	0.07	29.74
2500	198	0.0965	0.3738	0.0000	0.47	188.11
10000	199	0.0698	0.1107	0.0000	0.18	18.05
10000	200	0.0529	0.0442	0.0000	0.10	9.72
10000	201	0.0410	0.0189	0.0000	0.06	5.99
2500	202	0.0650	0.0654	0.0000	0.13	52.14
2500	203	0.0334	0.1296	0.0000	0.16	65.21

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	204	0.0104	0.0098	0.0000	0.02	2.02
10000	205	0.0180	0.0178	0.0000	0.04	3.57
10000	206	0.0067	0.0098	0.0000	0.02	1.65
10000	207	0.0122	0.0185	0.0000	0.03	3.07
10000	208	0.0154	0.0223	0.0000	0.04	3.77
10000	209	0.1372	0.1380	0.0000	0.28	27.51
10000	210	0.5078	0.4872	0.0000	0.99	99.50
10000	211	0.0315	0.0265	0.0000	0.06	5.80
10000	212	0.1672	0.1429	0.0000	0.31	31.00
10000	213	0.1846	0.0378	0.0000	0.22	22.24
10000	214	0.0194	0.0325	0.0000	0.05	5.19
10000	215	0.0166	0.0306	0.0000	0.05	4.72
10000	216	0.0104	0.0231	0.0000	0.03	3.34
10000	217	0.0106	0.0249	0.0000	0.04	3.55
10000	218	0.0380	0.0163	0.0000	0.05	5.43
10000	219	0.0832	0.0450	0.0000	0.13	12.81
10000	220	0.0391	0.0268	0.0000	0.07	6.60
10000	221	0.0094	0.0268	0.0000	0.04	3.63
10000	222	0.0074	0.0208	0.0000	0.03	2.82
10000	223	0.0071	0.0117	0.0000	0.02	1.89

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	224	0.0106	0.0178	0.0000	0.03	2.84
10000	225	0.0203	0.0605	0.0000	0.08	8.07
10000	226	0.3178	0.2793	0.0000	0.60	59.71
10000	227	0.2799	0.2623	0.0000	0.54	54.22
10000	228	0.0030	0.0068	0.0000	0.01	0.98
10000	229	0.0756	0.0571	0.0000	0.13	13.26
10000	230	0.0060	0.0163	0.0000	0.02	2.22
10000	231	0.0200	0.0246	0.0000	0.04	4.46
10000	232	0.0262	0.0280	0.0000	0.05	5.42
10000	233	0.0239	0.0223	0.0000	0.05	4.62
10000	234	0.0285	0.0212	0.0000	0.05	4.97
10000	235	0.0180	0.0200	0.0000	0.04	3.80
10000	236	0.0134	0.0204	0.0000	0.03	3.38
10000	237	0.0044	0.0068	0.0000	0.01	1.12
10000	238	0.0180	0.0302	0.0000	0.05	4.82
10000	239	0.1471	0.1512	0.0000	0.30	29.83
10000	240	0.3586	0.2347	0.0000	0.59	59.33
10000	241	0.0488	0.0295	0.0000	0.08	7.83
10000	242	0.0120	0.0272	0.0000	0.04	3.92
10000	243	0.2551	0.3001	0.0000	0.56	55.52

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
10000	244	0.4389	0.4925	0.0000	0.93	93.13
10000	245	0.0120	0.0166	0.0000	0.03	2.86
10000	246	0.0352	0.0363	0.0000	0.07	7.15
10000	247	0.0166	0.0310	0.0000	0.05	4.76
10000	248	0.0182	0.0295	0.0000	0.05	4.77
10000	249	0.0182	0.0295	0.0000	0.05	4.77
10000	250	0.0283	0.0578	0.0000	0.09	8.62
10000	251	0.0306	0.0903	0.0000	0.12	12.10
10000	252	0.5445	0.5650	0.0000	1.11	110.95
10000	253	0.7001	0.6992	0.0000	1.40	139.93
10000	254	0.0083	0.0181	0.0000	0.03	2.64
10000	255	0.0046	0.0125	0.0000	0.02	1.71
10000	256	0.0069	0.0147	0.0000	0.02	2.17
250000	257	0.5142	0.6436	0.0000	1.16	4.63
10000	258	0.0134	0.0076	0.0000	0.02	2.09
10000	259	0.0244	0.0408	0.0000	0.07	6.52
10000	260	0.0214	0.0325	0.0000	0.05	5.39
10000	261	0.0304	0.0272	0.0000	0.06	5.76
10000	262	0.0651	0.0208	0.0000	0.09	8.59
10000	263	0.1138	0.1330	0.0000	0.25	24.68

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	264	0.0615	0.0593	0.0000	0.12	12.08
10000	265	0.0069	0.0163	0.0000	0.02	2.32
10000	266	0.0509	0.0034	0.0000	0.05	5.43
10000	267	0.1950	0.1054	0.0000	0.30	30.04
10000	268	0.0435	0.0571	0.0000	0.10	10.06
10000	269	0.0403	0.0567	0.0000	0.10	9.70
10000	270	0.2418	0.1780	0.0000	0.42	41.98
10000	271	0.2925	0.1327	0.0000	0.43	42.52
10000	272	0.1710	0.0283	0.0000	0.20	19.93
10000	273	0.9087	0.9169	0.0000	1.83	182.56
10000	275	0.1779	0.1746	0.0000	0.35	35.25
10000	276	0.0069	0.0197	0.0000	0.03	2.66
10000	277	0.0145	0.0129	0.0000	0.03	2.74
10000	278	0.0150	0.0272	0.0000	0.04	4.22
10000	279	0.0161	0.0261	0.0000	0.04	4.22
10000	280	0.0203	0.0370	0.0000	0.06	5.73
10000	281	0.0440	0.0249	0.0000	0.07	6.89
10000	282	0.0822	0.0336	0.0000	0.12	11.58
10000	283	0.1872	0.1822	0.0000	0.37	36.94
10000	284	0.0030	0.0042	0.0000	0.01	0.72

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
10000	285	0.0078	0.0253	0.0000	0.03	3.32
2500	286	0.2231	0.1901	0.0000	0.41	165.26
2500	287	0.3872	0.3394	0.0000	0.73	290.63
2500	288	0.8167	0.8500	0.0000	1.67	666.69
2500	289	0.8414	0.9294	0.0000	1.77	708.30
2500	290	0.5658	0.6077	0.0000	1.17	469.43
2500	291	0.2304	0.0042	0.0000	0.23	93.81
2500	292	0.0617	0.0763	0.0000	0.14	55.22
2500	293	0.1683	0.0998	0.0000	0.27	107.21
2500	294	0.2746	0.2627	0.0000	0.54	214.91
2500	295	0.3724	0.2835	0.0000	0.66	262.35
2500	296	0.0069	0.0204	0.0000	0.03	10.93
2500	297	0.0377	0.0204	0.0000	0.06	23.26
2500	298	0.0884	0.0204	0.0000	0.11	43.51
2500	299	0.6246	0.3371	0.0000	0.96	384.70
10000	300	0.0071	0.0159	0.0000	0.02	2.30
10000	301	0.2659	0.3481	0.0000	0.61	61.40
10000	302	0.0283	0.0140	0.0000	0.04	4.23
10000	303	0.0569	0.0476	0.0000	0.10	10.45
10000	304	0.2097	0.1187	0.0000	0.33	32.84

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	305	0.5997	0.5242	0.0000	1.12	112.39
10000	306	0.8984	0.6145	0.0000	1.51	151.29
10000	307	0.0709	0.0147	0.0000	0.09	8.56
10000	308	0.0592	0.0412	0.0000	0.10	10.03
10000	309	0.0378	0.0608	0.0000	0.10	9.86
2500	310	0.0005	0.0026	0.0000	0.00	1.24
2500	311	0.4065	0.3345	0.0000	0.74	296.38
2500	312	0.6076	0.4464	0.0000	1.05	421.59
2500	315	0.2925	0.1073	0.0000	0.40	159.94
2500	316	0.1996	0.2151	0.0000	0.41	165.85
10000	317	0.0069	0.0147	0.0000	0.02	2.17
10000	318	0.0081	0.0159	0.0000	0.02	2.39
10000	319	0.0194	0.0257	0.0000	0.05	4.51
10000	320	0.0247	0.0359	0.0000	0.06	6.06
10000	321	0.4314	0.4713	0.0000	0.90	90.27
10000	322	0.7606	0.6939	0.0000	1.45	145.45
10000	323	0.0071	0.0117	0.0000	0.02	1.89
10000	324	0.0378	0.0193	0.0000	0.06	5.70
10000	325	0.2087	0.0272	0.0000	0.24	23.59
10000	326	0.3077	0.0026	0.0000	0.31	31.03

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	327	0.1758	0.0000	0.0000	0.18	17.58
2500	329	0.5591	0.3583	0.0000	0.92	366.95
2500	331	0.1981	0.2714	0.0000	0.47	187.78
2500	332	0.1150	0.2528	0.0000	0.37	147.15
10000	333	0.0085	0.0181	0.0000	0.03	2.67
10000	334	0.0154	0.0351	0.0000	0.05	5.06
10000	335	0.0154	0.0200	0.0000	0.04	3.55
10000	336	0.0235	0.0253	0.0000	0.05	4.88
10000	337	0.0359	0.0767	0.0000	0.11	11.27
10000	338	0.0242	0.0540	0.0000	0.08	7.82
10000	339	0.2560	0.2445	0.0000	0.50	50.05
10000	340	0.5696	0.5507	0.0000	1.12	112.02
10000	341	0.0104	0.0193	0.0000	0.03	2.96
10000	342	0.0672	0.1236	0.0000	0.19	19.08
10000	343	0.2882	0.1584	0.0000	0.45	44.65
2500	344	0.0426	0.0000	0.0000	0.04	17.03
2500	345	0.1233	0.3258	0.0000	0.45	179.63
2500	346	0.5814	0.6784	0.0000	1.26	503.93
2500	347	0.2244	0.0000	0.0000	0.22	89.75
2500	349	0.3458	0.6784	0.0000	1.02	409.67

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
2500	350	0.4890	0.8330	0.0000	1.32	528.79
10000	351	0.0071	0.0155	0.0000	0.02	2.26
10000	352	0.0074	0.0163	0.0000	0.02	2.36
10000	353	0.0085	0.0147	0.0000	0.02	2.33
10000	354	0.0085	0.0117	0.0000	0.02	2.02
10000	355	0.0223	0.0472	0.0000	0.07	6.96
10000	356	0.1608	0.0790	0.0000	0.24	23.97
10000	357	0.0951	0.1153	0.0000	0.21	21.04
10000	358	0.0164	0.0299	0.0000	0.05	4.62
10000	359	0.0596	0.0797	0.0000	0.14	13.94
10000	360	0.0988	0.1236	0.0000	0.22	22.23
10000	361	0.3625	0.2525	0.0000	0.62	61.50
10000	362	1.6124	0.9003	0.0000	2.51	251.26
2500	363	0.0909	0.1742	0.0000	0.27	106.07
2500	364	0.4652	0.5223	0.0000	0.99	395.00
2500	365	0.7256	0.4959	0.0000	1.22	488.58
2500	366	1.3017	0.6992	0.0000	2.00	800.35
2500	367	0.3833	0.2056	0.0000	0.59	235.57
2500	368	0.3904	0.3556	0.0000	0.75	298.40
2500	369	0.4622	0.5484	0.0000	1.01	404.24

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
2500	370	1.3732	1.2211	0.0000	2.59	1037.75
2500	371	1.9998	1.2332	0.0000	3.23	1293.22
2500	372	1.5791	1.2189	0.0000	2.80	1119.18
2500	373	1.4849	0.9910	0.0000	2.48	990.35
10000	374	0.0074	0.0151	0.0000	0.02	2.25
10000	375	0.1076	0.0922	0.0000	0.20	19.98
10000	376	0.0071	0.0121	0.0000	0.02	1.92
10000	377	0.0136	0.0242	0.0000	0.04	3.78
10000	378	0.0076	0.0110	0.0000	0.02	1.86
10000	379	0.0456	0.0246	0.0000	0.07	7.01
10000	380	0.0090	0.0163	0.0000	0.03	2.52
10000	381	0.0106	0.0200	0.0000	0.03	3.06
10000	382	0.0270	0.0499	0.0000	0.08	7.68
10000	383	0.0092	0.0163	0.0000	0.03	2.55
10000	384	0.0000	0.0000	0.0000	0.00	0.00
10000	385	0.1961	0.0707	0.0000	0.27	26.68
2500	386	0.2275	0.4350	0.0000	0.66	264.99
2500	387	0.8417	0.6096	0.0000	1.45	580.53
2500	388	1.0972	0.7162	0.0000	1.81	725.36
2500	389	0.9374	0.6115	0.0000	1.55	619.55

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
2500	390	0.4505	0.8035	0.0000	1.25	501.62
2500	391	0.3980	0.6497	0.0000	1.05	419.08
2500	392	0.2739	0.3288	0.0000	0.60	241.09
2500	393	0.2063	0.2631	0.0000	0.47	187.72
2500	394	0.3775	0.3526	0.0000	0.73	292.05
2500	395	0.2995	0.5386	0.0000	0.84	335.24
2500	396	0.7200	0.6765	0.0000	1.40	558.62
2500	397	0.7612	0.6765	0.0000	1.44	575.09
2500	398	0.7701	0.4619	0.0000	1.23	492.78
2500	399	0.4907	0.4751	0.0000	0.97	386.32
2500	400	0.2739	0.3288	0.0000	0.60	241.09
10000	401	0.0071	0.0144	0.0000	0.02	2.15
10000	402	0.0044	0.0083	0.0000	0.01	1.27
10000	403	0.0193	0.0412	0.0000	0.06	6.05
10000	404	0.0299	0.0098	0.0000	0.04	3.98
10000	405	0.0589	0.0355	0.0000	0.09	9.45
10000	406	0.0058	0.0102	0.0000	0.02	1.60
10000	407	0.0044	0.0117	0.0000	0.02	1.61
10000	408	0.0062	0.0147	0.0000	0.02	2.10
10000	409	0.0044	0.0076	0.0000	0.01	1.19

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	410	0.1411	0.2321	0.0000	0.37	37.32
10000	411	0.0000	0.0000	0.0000	0.00	0.00
10000	412	0.0205	0.0665	0.0000	0.09	8.70
10000	413	0.3392	0.1134	0.0000	0.45	45.26
2500	414	0.0803	0.0283	0.0000	0.11	43.47
2500	415	0.0803	0.1107	0.0000	0.19	76.43
2500	416	0.4350	0.3995	0.0000	0.83	333.81
2500	417	0.2739	0.3288	0.0000	0.60	241.09
2500	418	0.6481	0.4751	0.0000	1.12	449.29
2500	419	0.4405	0.4018	0.0000	0.84	336.92
10000	420	1.0963	0.5809	0.0000	1.68	167.72
10000	421	0.2960	0.2128	0.0000	0.51	50.87
10000	422	0.0523	0.0495	0.0000	0.10	10.18
2500	423	0.0495	0.0900	0.0000	0.14	55.78
2500	424	0.2709	0.2502	0.0000	0.52	208.45
2500	425	0.1786	0.0000	0.0000	0.18	71.43
2500	426	0.2308	0.2676	0.0000	0.50	199.36
2500	427	0.1425	0.1765	0.0000	0.32	127.61
2500	428	0.1522	0.1825	0.0000	0.33	133.88
250000	429	0.3573	0.4898	0.0000	0.85	3.39

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
250000	430	0.5639	0.5737	0.0000	1.14	4.55
250000	431	0.3642	0.6006	0.0000	0.96	3.86
250000	432	2.6367	1.8773	0.0000	4.51	18.06
250000	433	2.8053	2.2322	0.0000	5.04	20.15
250000	434	1.9859	1.5016	0.0000	3.49	13.95
10000	435	0.1084	0.0370	0.0000	0.15	14.54
10000	436	0.0154	0.0094	0.0000	0.02	2.49
10000	437	0.0716	0.0563	0.0000	0.13	12.79
10000	438	0.0081	0.0174	0.0000	0.03	2.54
10000	439	0.0101	0.0234	0.0000	0.03	3.36
10000	440	0.0012	0.0023	0.0000	0.00	0.34
10000	441	0.0131	0.0295	0.0000	0.04	4.26
10000	442	0.0060	0.0185	0.0000	0.02	2.45
10000	443	0.1511	0.1104	0.0000	0.26	26.15
10000	444	0.0058	0.0140	0.0000	0.02	1.97
10000	445	0.0012	0.0019	0.0000	0.00	0.30
10000	446	0.0058	0.0144	0.0000	0.02	2.01
10000	447	0.0041	0.0102	0.0000	0.01	1.44
10000	448	0.0028	0.0072	0.0000	0.01	0.99
10000	449	0.0016	0.0042	0.0000	0.01	0.58

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	450	0.0104	0.0189	0.0000	0.03	2.93
10000	451	0.1010	0.0178	0.0000	0.12	11.88
10000	452	0.1277	0.0238	0.0000	0.15	15.15
10000	453	0.2998	0.1935	0.0000	0.49	49.33
10000	454	0.0431	0.0389	0.0000	0.08	8.20
10000	455	0.0060	0.0144	0.0000	0.02	2.04
10000	456	0.0055	0.0129	0.0000	0.02	1.84
10000	457	0.0055	0.0136	0.0000	0.02	1.91
10000	458	0.0051	0.0110	0.0000	0.02	1.60
10000	459	0.0025	0.0064	0.0000	0.01	0.90
10000	460	0.0014	0.0045	0.0000	0.01	0.59
10000	461	0.0081	0.0159	0.0000	0.02	2.39
10000	462	0.0104	0.0163	0.0000	0.03	2.66
10000	463	0.0191	0.0348	0.0000	0.05	5.39
10000	464	0.1651	0.0884	0.0000	0.25	25.35
10000	465	0.3210	0.2457	0.0000	0.57	56.67
10000	466	0.3626	0.2264	0.0000	0.59	58.90
10000	467	0.0700	0.0155	0.0000	0.09	8.55
10000	468	0.0244	0.0465	0.0000	0.07	7.09
10000	469	0.0735	0.0590	0.0000	0.13	13.24

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
10000	470	0.0253	0.0442	0.0000	0.07	6.96
10000	471	0.0173	0.0382	0.0000	0.06	5.55
10000	472	0.3779	0.3640	0.0000	0.74	74.18
10000	473	0.4046	0.3621	0.0000	0.77	76.66
10000	474	0.0012	0.0023	0.0000	0.00	0.34
10000	475	0.0076	0.0151	0.0000	0.02	2.27
10000	476	0.0834	0.0658	0.0000	0.15	14.92
10000	477	0.0101	0.0204	0.0000	0.03	3.05
10000	478	0.0818	0.0820	0.0000	0.16	16.38
10000	479	0.0171	0.0472	0.0000	0.06	6.43
10000	480	0.0115	0.0242	0.0000	0.04	3.57
10000	481	0.0028	0.0068	0.0000	0.01	0.96
10000	482	0.0824	0.0144	0.0000	0.10	9.68
10000	483	0.1198	0.0767	0.0000	0.20	19.65
10000	484	0.1264	0.0472	0.0000	0.17	17.36
10000	485	0.0661	0.0646	0.0000	0.13	13.07
10000	486	0.2136	0.1739	0.0000	0.39	38.75
10000	487	0.1349	0.0790	0.0000	0.21	21.39
10000	488	0.0622	0.0336	0.0000	0.10	9.58
10000	489	0.1073	0.0865	0.0000	0.19	19.39

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
250000	490	0.6588	0.7831	0.0000	1.44	5.77
250000	491	0.2428	0.3148	0.0000	0.56	2.23
250000	492	0.5915	0.8213	0.0000	1.41	5.65
250000	493	2.2969	1.2257	0.0000	3.52	14.09
250000	494	0.4371	0.5401	0.0222	1.00	4.00
250000	495	0.5304	0.6758	0.0000	1.21	4.82
250000	496	0.1762	0.2657	0.0934	0.54	2.14
250000	497	0.1566	0.2294	0.0000	0.39	1.54
250000	498	0.2487	0.3277	0.0000	0.58	2.31
250000	499	0.8504	0.6856	0.0000	1.54	6.14
250000	500	0.1214	0.1130	0.0000	0.23	0.94
250000	501	0.0062	0.0094	0.0000	0.02	0.06
250000	502	0.0219	0.0404	0.0000	0.06	0.25
250000	503	0.5202	0.3693	0.0474	0.94	3.75
250000	504	0.0730	0.1107	0.0113	0.20	0.78
250000	505	0.0654	0.1247	0.0113	0.20	0.81
250000	506	0.1422	0.1232	0.0241	0.29	1.16
250000	507	0.0283	0.0540	0.0000	0.08	0.33
250000	508	0.6407	0.6145	0.0039	1.26	5.04
250000	509	0.5575	0.6297	0.0000	1.19	4.75

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
250000	510	0.6447	0.4959	0.0000	1.14	4.56
250000	511	0.5756	0.5303	0.0000	1.11	4.42
250000	512	0.0513	0.0336	0.0000	0.08	0.34
250000	513	0.0253	0.0253	0.0000	0.05	0.20
250000	514	0.5019	0.1542	0.0105	0.67	2.67
250000	515	0.0843	0.1380	0.0105	0.23	0.93
250000	516	0.3350	0.2324	0.0109	0.58	2.31
250000	517	0.0177	0.0314	0.0004	0.05	0.20
250000	518	0.0385	0.0949	0.0004	0.13	0.53
250000	519	0.1545	0.1644	0.0000	0.32	1.28
250000	520	0.4505	0.4074	0.0000	0.86	3.43
10000	521	0.0479	0.0265	0.0000	0.07	7.43
10000	522	0.1167	0.1081	0.0000	0.22	22.48
10000	523	0.0930	0.0703	0.0000	0.16	16.33
10000	524	0.5365	0.7328	0.0000	1.27	126.93
10000	525	0.0051	0.0094	0.0000	0.01	1.45
10000	526	0.0187	0.0310	0.0000	0.05	4.96
10000	527	0.0274	0.0359	0.0000	0.06	6.33
10000	528	0.0143	0.0265	0.0000	0.04	4.07
10000	529	0.0778	0.1145	0.0000	0.19	19.23

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
10000	530	0.3881	0.2219	0.0000	0.61	60.99
10000	531	2.1210	1.7945	0.0000	3.92	391.55
10000	532	0.2944	0.3024	0.0000	0.60	59.67
10000	533	0.2221	0.0389	0.0000	0.26	26.10
10000	534	0.1278	0.0624	0.0000	0.19	19.01
10000	535	0.0111	0.0197	0.0000	0.03	3.07
10000	538	0.5566	0.4887	0.0000	1.05	104.53
10000	539	0.3614	0.2033	0.0000	0.56	56.47
10000	540	0.2021	0.0586	0.0000	0.26	26.07
10000	541	0.0364	0.0548	0.0000	0.09	9.12
250000	542	0.9286	0.5499	0.0000	1.48	5.91
250000	543	0.2137	0.2200	0.0000	0.43	1.73
250000	544	0.0025	0.0064	0.0000	0.01	0.04
250000	545	0.0154	0.0265	0.0000	0.04	0.17
250000	546	0.1938	0.0847	0.0000	0.28	1.11
250000	547	0.0136	0.0147	0.0000	0.03	0.11
250000	548	0.0076	0.0110	0.0105	0.03	0.12
250000	549	0.0113	0.0178	0.0000	0.03	0.12
250000	550	0.2123	0.1402	0.0105	0.36	1.45
250000	551	0.0035	0.0045	0.0004	0.01	0.03

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
250000	552	0.0002	0.0008	0.0004	0.00	0.01
250000	553	0.2596	0.2978	0.0004	0.56	2.23
250000	554	0.3965	0.2778	0.0625	0.74	2.95
250000	555	0.0970	0.0722	0.0000	0.17	0.68
250000	556	0.1487	0.0491	0.0000	0.20	0.79
250000	557	0.2283	0.2022	0.0069	0.44	1.75
250000	558	0.2434	0.1323	0.0130	0.39	1.55
250000	559	0.2227	0.2547	0.0158	0.49	1.97
10000	566	0.0012	0.0026	0.0000	0.00	0.38
10000	569	0.7354	0.7544	0.0000	1.49	148.98
10000	570	0.0062	0.0076	0.0000	0.01	1.38
10000	571	0.0378	0.0231	0.0000	0.06	6.08
10000	572	0.0742	0.0801	0.0000	0.15	15.43
10000	573	0.0327	0.0344	0.0000	0.07	6.71
10000	574	0.0251	0.0306	0.0000	0.06	5.57
250000	575	0.2241	0.0858	0.0000	0.31	1.24
250000	576	0.7284	0.5934	0.0465	1.37	5.47
250000	577	0.2584	0.1803	0.0465	0.49	1.94
250000	578	0.0870	0.0480	0.0000	0.14	0.54
250000	579	0.0345	0.0049	0.0000	0.04	0.16

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
10000	580	0.0025	0.0034	0.0000	0.01	0.59
10000	581	0.0569	0.0506	0.0314	0.14	13.89
10000	582	0.9098	0.7597	0.0314	1.70	170.09
10000	583	0.0000	0.0000	0.0000	0.00	0.00
10000	584	0.0465	0.0038	0.0000	0.05	5.03
10000	585	0.0387	0.0038	0.0000	0.04	4.24
10000	586	0.0025	0.0038	0.0000	0.01	0.63
1000000	587	0.0838	0.0094	0.0000	0.09	0.09
250000	588	0.0000	0.0000	0.0000	0.00	0.00
250000	591	0.0189	0.0238	0.0158	0.06	0.23
250000	592	0.3770	0.3938	0.0000	0.77	3.08
250000	593	0.0173	0.0238	0.0000	0.04	0.16
250000	594	0.0854	0.0174	0.0000	0.10	0.41
250000	595	0.0037	0.0053	0.0000	0.01	0.04
250000	598	0.0062	0.0087	0.0158	0.03	0.12
250000	599	0.0062	0.0087	0.0158	0.03	0.12
250000	600	0.0062	0.0087	0.0000	0.01	0.06
250000	601	0.0099	0.0151	0.2675	0.29	1.17
250000	602	0.1446	0.1293	0.0132	0.29	1.15
1000000	603	0.0537	0.0850	1.0569	1.20	1.20

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density
from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
1000000	604	0.1006	0.0627	0.0249	0.19	0.19
1000000	605	0.0567	0.0620	0.0624	0.18	0.18
250000	606	0.0062	0.0087	0.0158	0.03	0.12
250000	607	0.0166	0.0227	0.0158	0.06	0.22
250000	608	0.0065	0.0098	0.0158	0.03	0.13
250000	609	0.0122	0.0204	0.0000	0.03	0.13
250000	610	0.2852	0.1965	0.0000	0.48	1.93
250000	611	0.0154	0.0215	0.0000	0.04	0.15
250000	612	0.0025	0.0045	0.0000	0.01	0.03
250000	613	0.0039	0.0068	0.0000	0.01	0.04
250000	614	0.0389	0.0102	0.0000	0.05	0.20
250000	615	0.1426	0.2460	2.8877	3.28	13.11
1000000	616	0.0233	0.0253	0.0000	0.05	0.05
250000	617	0.0000	0.0000	0.0000	0.00	0.00
250000	618	0.0000	0.0000	0.0000	0.00	0.00
250000	619	0.4460	0.0488	0.2154	0.71	2.84
250000	620	0.0861	0.0000	0.0000	0.09	0.34
250000	623	0.0670	0.0000	0.0000	0.07	0.27
250000	624	0.1297	0.0737	0.0133	0.22	0.87
1000000	627	0.1482	0.0333	0.0976	0.28	0.28

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
250000	628	0.2053	0.0125	0.1435	0.36	1.45
250000	629	0.0090	0.0042	0.0000	0.01	0.05
250000	630	0.0030	0.0042	0.0000	0.01	0.03
250000	631	0.0030	0.0042	0.0000	0.01	0.03
250000	632	0.0030	0.0042	0.0000	0.01	0.03
250000	633	0.0030	0.0042	0.0000	0.01	0.03
250000	634	0.0030	0.0042	0.0000	0.01	0.03
250000	635	0.0030	0.0042	0.0000	0.01	0.03
250000	636	0.0030	0.0042	0.0000	0.01	0.03
1000000	640	0.0012	0.0000	0.0000	0.00	0.00
1000000	644	0.0106	0.0042	0.2766	0.29	0.29
1000000	647	0.0074	0.0102	0.0000	0.02	0.02
1000000	648	0.0041	0.0000	0.0000	0.00	0.00
1000000	649	0.0012	0.0011	0.0000	0.00	0.00
1000000	650	0.0088	0.0140	0.0000	0.02	0.02
1000000	653	0.0972	0.0941	0.0000	0.19	0.19
1000000	654	0.1877	0.1587	0.6042	0.95	0.95
1000000	655	0.1327	0.0756	0.1385	0.35	0.35
1000000	656	0.1353	0.0189	0.0000	0.15	0.15
10000	657	0.0088	0.0136	0.0000	0.02	2.24

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR)			TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
		MOBILE	RES.WOOD	FOR.FIRE		
10000	658	0.0779	0.0722	0.0000	0.15	15.01
10000	659	0.1410	0.1213	0.0000	0.26	26.23
10000	660	0.0221	0.0193	0.0000	0.04	4.14
10000	661	0.0977	0.0639	0.0000	0.16	16.15
10000	662	1.0984	0.8545	0.0000	1.95	195.29
10000	663	0.0074	0.0113	0.0000	0.02	1.87
10000	665	0.1527	0.1179	0.0000	0.27	27.06
10000	666	0.0214	0.0000	0.0000	0.02	2.14
10000	667	0.0189	0.0000	0.0000	0.02	1.89
250000	683	0.0474	0.0060	0.0000	0.05	0.21
1000000	684	0.1193	0.0782	0.0319	0.23	0.23
1000000	685	0.1635	0.0922	1.0569	1.31	1.31
1000000	686	0.1027	0.0586	0.0000	0.16	0.16
250000	688	0.0755	0.0548	0.0108	0.14	0.56
1000000	689	0.3250	0.2831	4.3276	4.94	4.94
1000000	690	0.3691	0.1489	0.2458	0.76	0.76
1000000	691	0.1515	0.0952	8.2075	8.45	8.45
1000000	692	0.0062	0.0117	1.0569	1.07	1.07
1000000	693	0.0122	0.0200	1.0569	1.09	1.09
1000000	694	0.0569	0.0272	1.0569	1.14	1.14

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
1000000	695	0.1099	0.1051	14.2953	14.51	14.51
1000000	696	0.0490	0.0302	0.0000	0.08	0.08
1000000	697	0.0071	0.0181	0.0000	0.03	0.03
1000000	698	0.0399	0.0998	41.5101	41.65	41.65
1000000	699	0.0071	0.0189	0.0000	0.03	0.03
1000000	700	0.0062	0.0170	0.0000	0.02	0.02
1000000	701	0.0000	0.0000	0.0000	0.00	0.00
1000000	702	0.0000	0.0000	0.0000	0.00	0.00
1000000	703	0.0048	0.0060	0.0000	0.01	0.01
1000000	706	0.0094	0.0185	0.0000	0.03	0.03
1000000	707	0.0060	0.0140	0.0000	0.02	0.02
1000000	708	0.0060	0.0159	0.0000	0.02	0.02
1000000	709	0.0009	0.0023	0.0000	0.00	0.00
1000000	710	0.0048	0.0117	0.0000	0.02	0.02
1000000	711	0.0002	0.0011	0.0000	0.00	0.00
1000000	717	0.0023	0.0053	0.0000	0.01	0.01
1000000	723	0.0000	0.0000	0.0000	0.00	0.00
1000000	724	0.0025	0.0049	0.0000	0.01	0.01
1000000	725	0.0035	0.0072	0.0000	0.01	0.01
1000000	726	0.0039	0.0079	0.0000	0.01	0.01

TABLE B1-2 (cont'd)

Regional Annual PAH Emissions and Emission Density from Three Major Sources to the Atmosphere in Ontario

GRID AREA (Ha)	UTM GRID	TOTAL PAH INVENTORY FOR EACH GRID AND SOURCE (MT/YEAR) MOBILE	RES.WOOD	FnOR.FIRE	TOTAL PAH (MT/YEAR)	EMISSION DENSITY (g/ha/y)
1000000	731	0.0023	0.0038	0.0000	0.01	0.01
1000000	732	0.0014	0.0030	0.0000	0.00	0.00
1000000	733	0.0025	0.0049	0.0000	0.01	0.01
1000000	740	0.0014	0.0023	0.0000	0.00	0.00
1000000	743	0.0012	0.0015	0.0000	0.00	0.00
	TOTAL	102.17	88.89	79.28	270.34	

TABLE B1-3

Colour Coding for Illustrative Regional PAH Maps

Colour Code	PAH Emission Density (g/ha/yr)
blue	<10
green	10-50
yellow	>50-100
red	>100-500
violet	>500

FIGURE B1-1

PAH Emission Densities for Southwestern Ontario

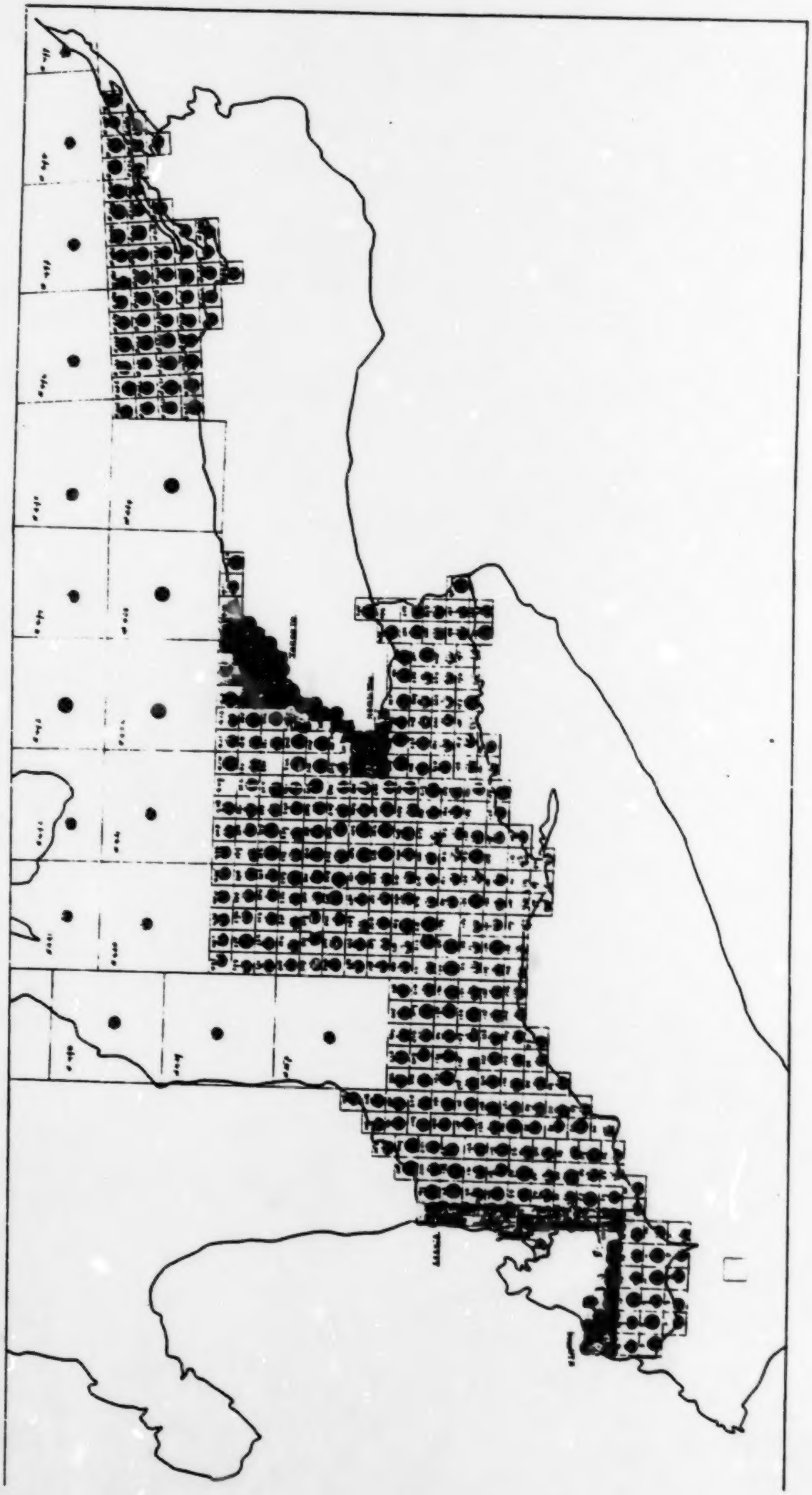

FIGURE B1-2

PAH Emission Densities for Southeastern Ontario

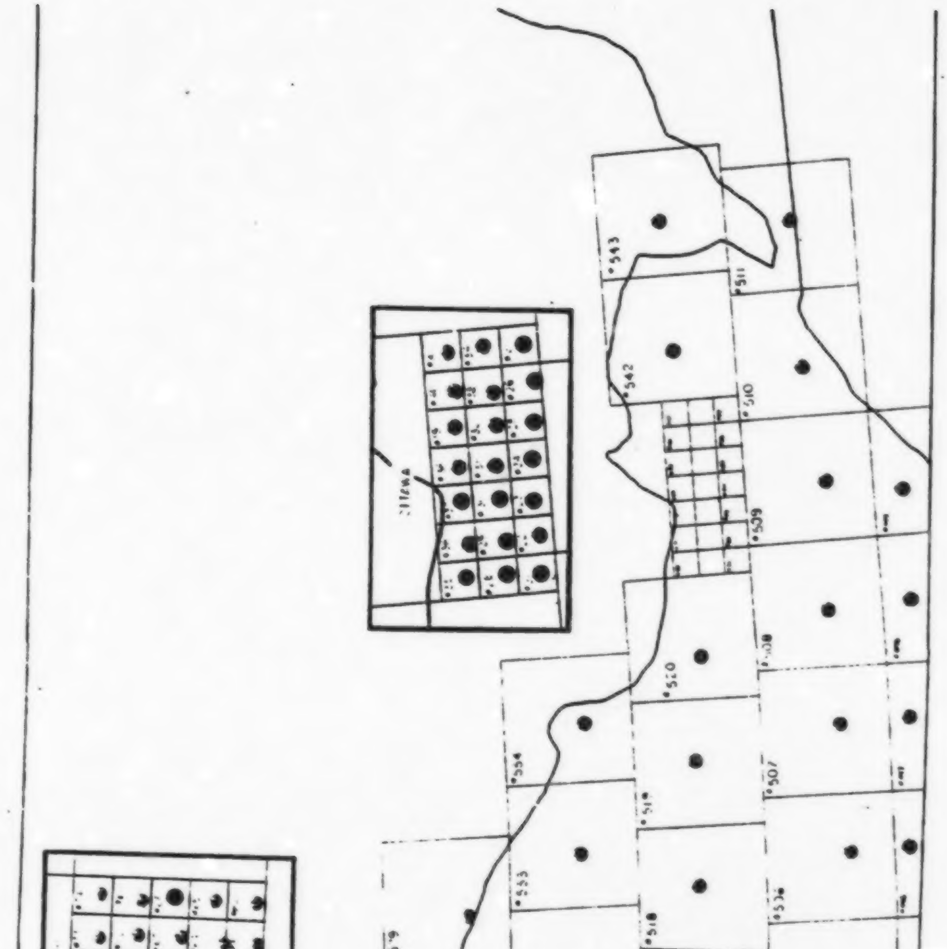

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FIGURE B1-3

PAH Emission Densities for Central Ontario

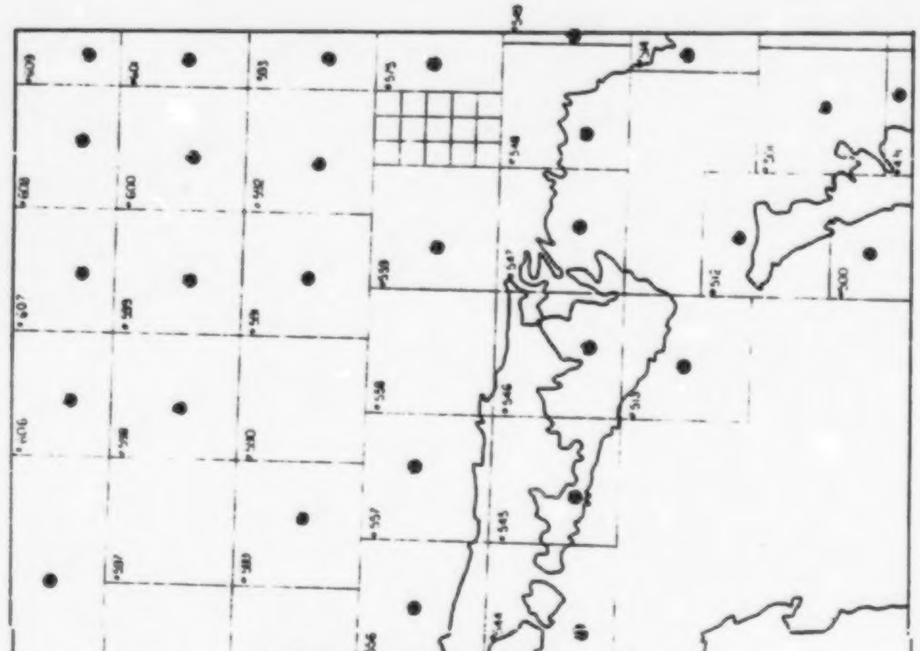
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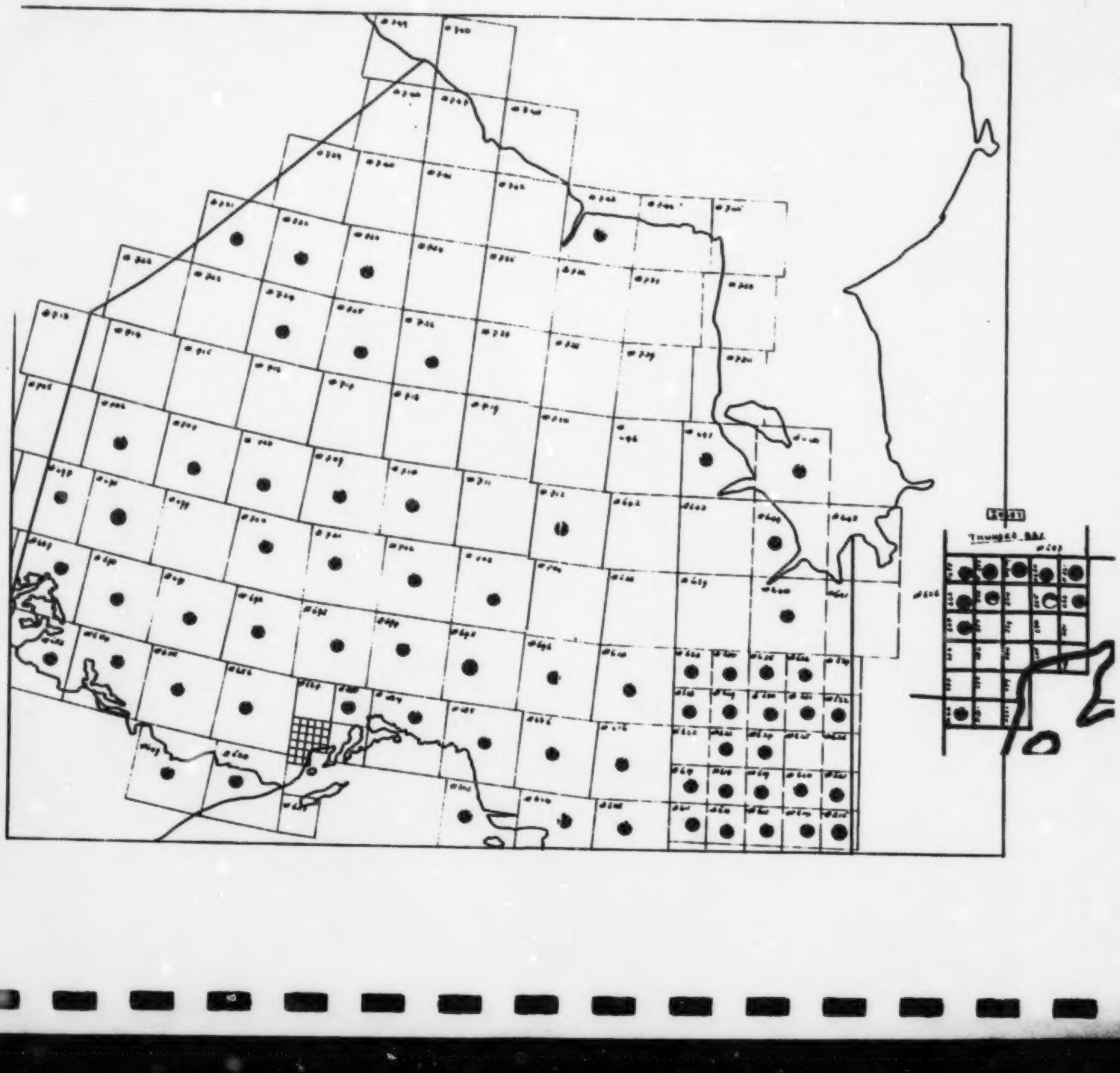
FIGURE B1-4

PAH Emission Densities for Northern Ontario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